Præsentation af SERC resultater

Mogensen, Mogens Bjerg

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2012

Præsentation af SERC resultater

Mogens Bjerg Mogensen

Institut for Energikonvertering og –lagring

Møde om Elektrokemi til grøn gas og andre grønne teknologier

Torsdag den 8. november 2012 kl. 13.00 – 17.00 i Ingeniørhuset (IDA) i København

SERC

SERC = Strategic Electrochemistry Research Center handler om forskning i elektrokemiske celler

Blandt andet brændselsceller, der kan producere elektricitet ud fra O_2 (+) og metan, CH_4, H_2, CO eller andre brændselsgasser (-)

og elektrolyseceller, der kan producere O_2 (+) og syntesegas (H_2 + CO) ud fra H_2O og CO_2 (-) samt elektricitet

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SERC

- **En elektrokemisk celle består af to elektroder adskilt af en elektrolyt**
- **En elektrolyt er en god ionleder og en elektronisolator**
- **En elektrode er som minimum en god elektronleder**
- **SERC har mest handlet om fastoxid celler – SOC (solid oxide cells), der består af udelukkende faste stoffer, mest af keramiske materialer**

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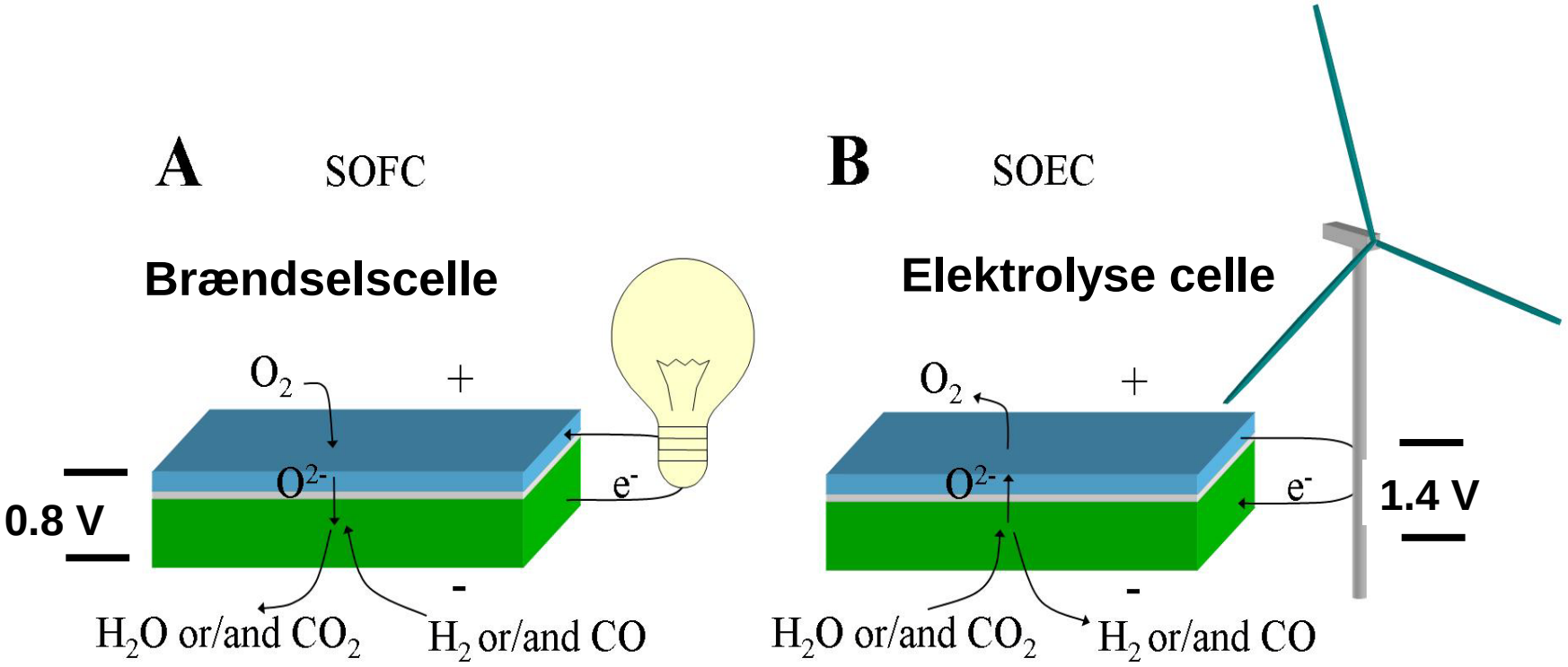
Princip af reversibel fastoxid celle SOC



600 - 900 °C **EMF ca. 1.1 V**

Samme celle kan køres som brændselscelle, SOFC (A), eller som elektrolysecelle, SOEC (B).

Ni -YSZ- understøttet SOC

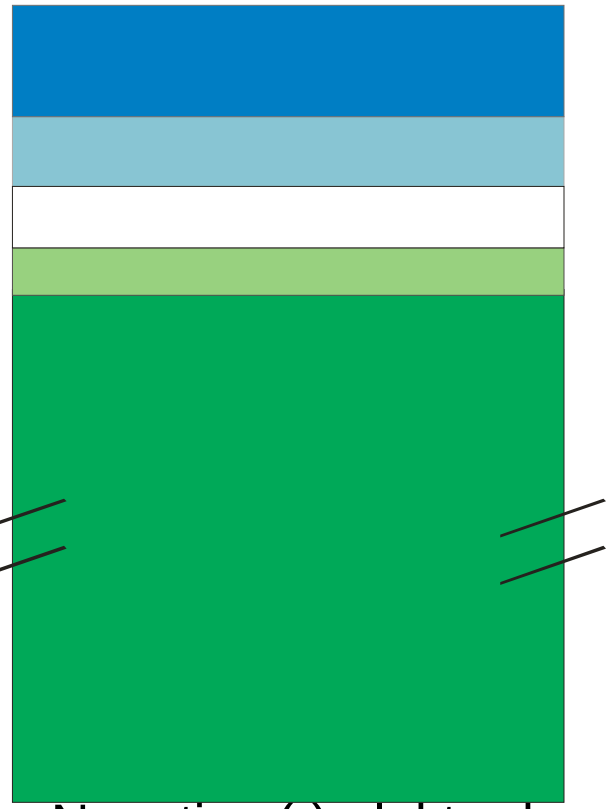
Strømsamler,
LSM, ~40 µm

Oxygen elektrode
LSM-YSZ, ~20 µm

Elektrolyt, YSZ, ~10 µm

Brændselselektrode
Ni-YSZ, ~15 µm

Strømsamler og support
Ni-YSZ, ~330 µm



LSM = $(La_{075}Sr_{0.25})_{0.95}MnO_3$

YSZ = $Zr_{0.84}Y_{0.16}O_{1.92}$

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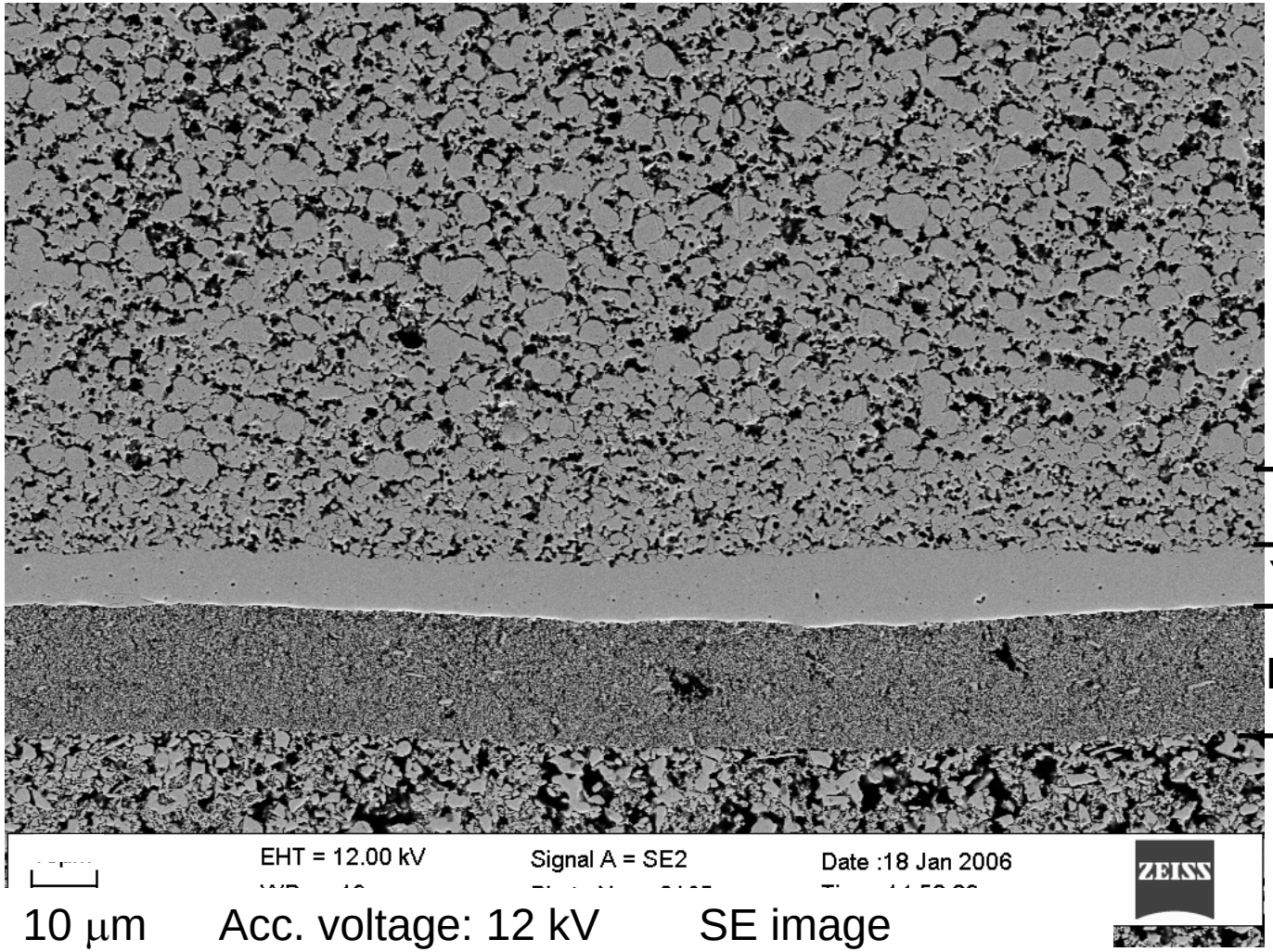
SEM af Ni-YSZ supporteret SOC



10 μm Acc. voltage: 12 kV SE image

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Ni-YSZ support

Ni-YSZ elektrode

YSZ elektrolyt

LSM-YSZ elektrode

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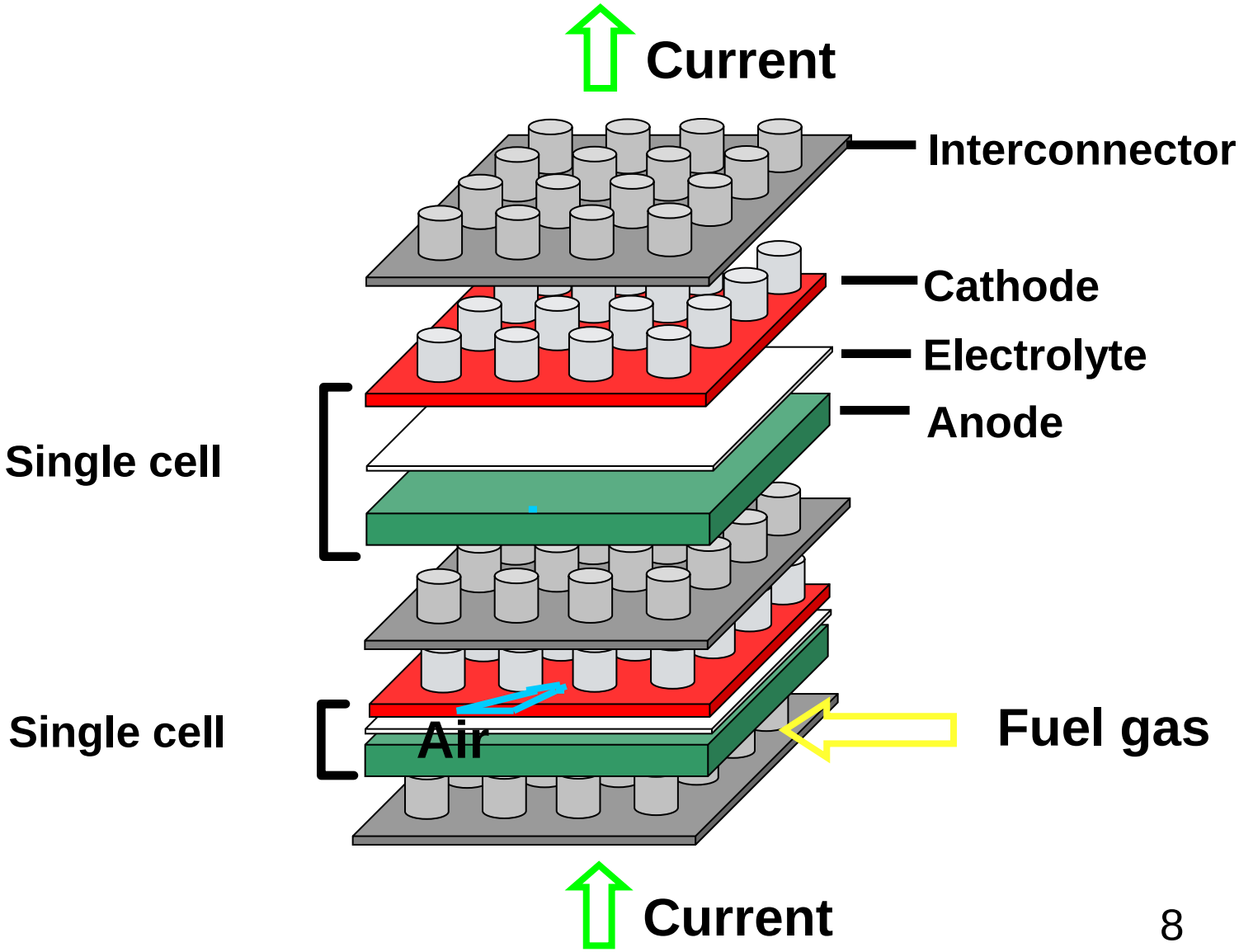
DTU Risø solid oxide cell (SOC)
12 x 12 cm^2

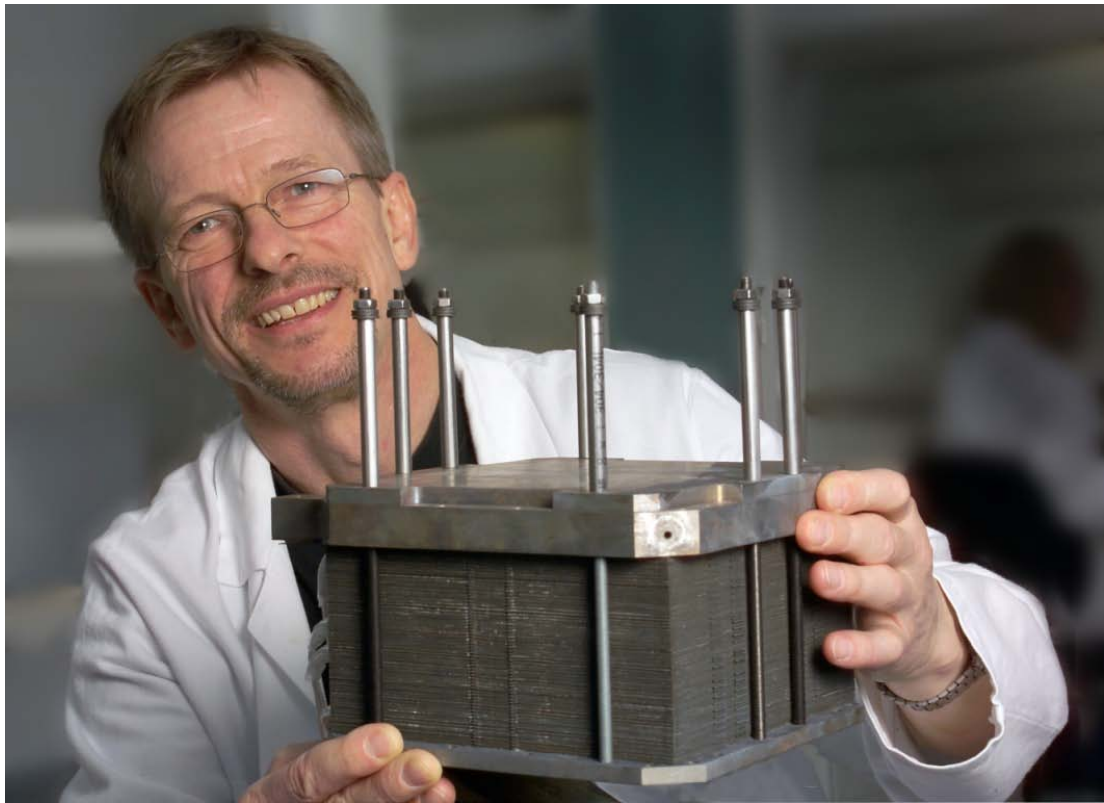
SERC

~ 1 V of each cell ⇒ cell stack of many cells

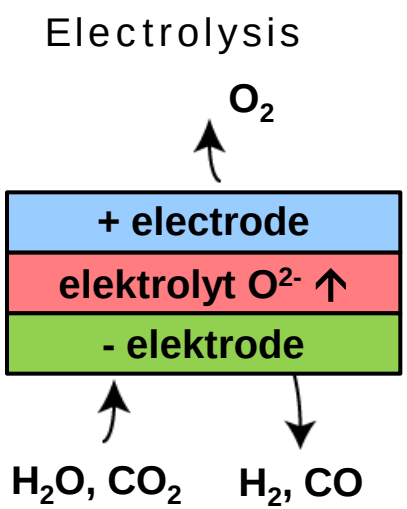


En rigtig celle stak

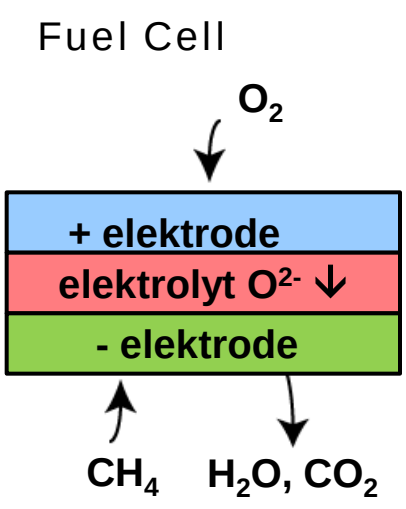
- **To operate at useful voltages several cells, e.g. 50, are stacked in series**
- **High energy density: Stack electric power density of ~3 kW/liter demonstrated with Topsoe cell stacks in electrolysis mode**
- **Scalable technology: From kW to MW**



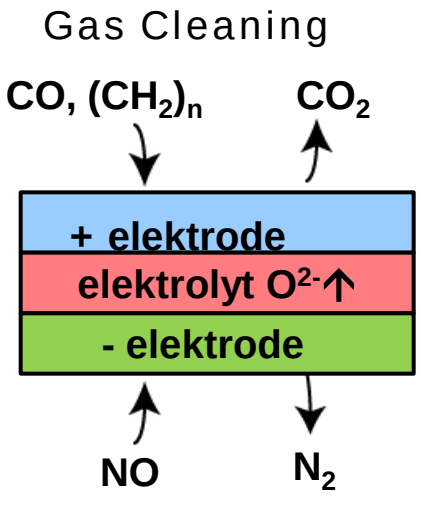
SERC er om anvendt elektrokemi



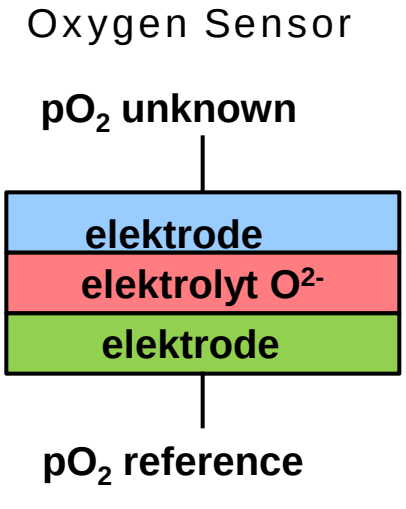
Electricity consumption
Syngas and oxygen production



Electricity production
Fuel gas and oxygen consumption



Gas purification using electricity
– pumping O^{2-}



Voltage is a measure of oxygen partial pressure

Celler af keramiske materialer – driftstemperatur 600 til 900 °C

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Formål og budget for SERC

1. **At udføre industrielt relevant forskning inden for elektrokemi på højt internationalt niveau**

2. **At uddanne kandidater og PhD'er samt træne postdocs (unge forskere)**

3. **At udveksle viden mellem DTU Energikonvertering, de andre universitetsinstitutter og industripartnerne**

Budget: 25.7 Mkr. fra DSF, BENMI; Total 51.4 Mkr.

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8 Active Industry Participants

Participants with a contributing budget

- **Dinex A/S – Henrik Christensen**
- **DME – Danish Micro Engineering A/S - Curt Sander**
- **DONG Energy A/S – Aksel Hauge Pedersen**
- **Haldor Topsøe A/S - John Bøgild Hansen**
- **IRD Fuel Cells A/S - Laila Grahl-Madsen**
- **PBI-Dansensor A/S - Rune Bech Abrahamsen**
- **Topsoe Fuel Cell A/S - Niels Christiansen**
- **Videometer A/S - Niels Christian Krieger Lassen**

6 Scandinavian University Institutes
3 Universities

Participants with a contributing budget

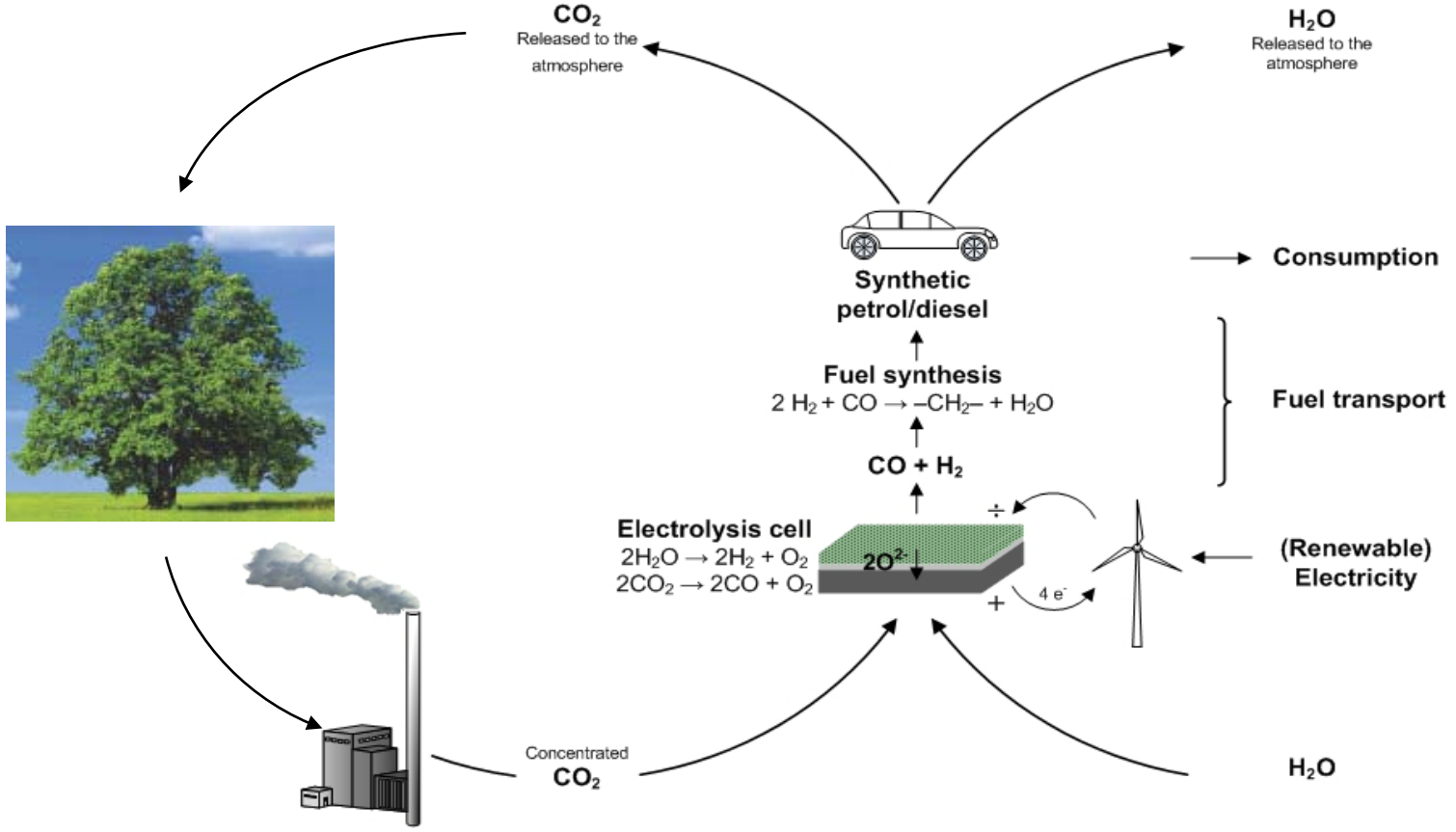
- **Department of Chemistry, DTU - Torben Jacobsen**
- **Department of Physics, DTU - Ib Chorkendorff and Jan Rossmeisl**
- **Department of Informatics and Mathematical Modeling, DTU - Rasmus Larsen**
- **Institute of Chemical Engineering, Biotechnology and Environmental Technology, SDU - Eivind Skou**
- **Polymer and Materials Chemistry, Lund University - Reine Wallenberg**
- **Risø DTU - Jacob Bowen, Kent Kammer Hansen, Karin Vels Hansen, Johan Hjelm, Mogens B. Mogensen**

International cooperation

1. University of Columbia, NY, USA, Klaus Lackner
2. Karlsruhe Institute of Technology, Ellen Ivers-Tiffée
3. University of St. Andrews, Scotland – John Irvine
4. University of Twente, NL – Henny Bouwmeester
5. Colorado School of Mines, Golden, CO, USA

Vision - Synthetic hydrocarbons from wind via pressurized electrolysis

Short term realisation - CO_2 capture from industrial sources



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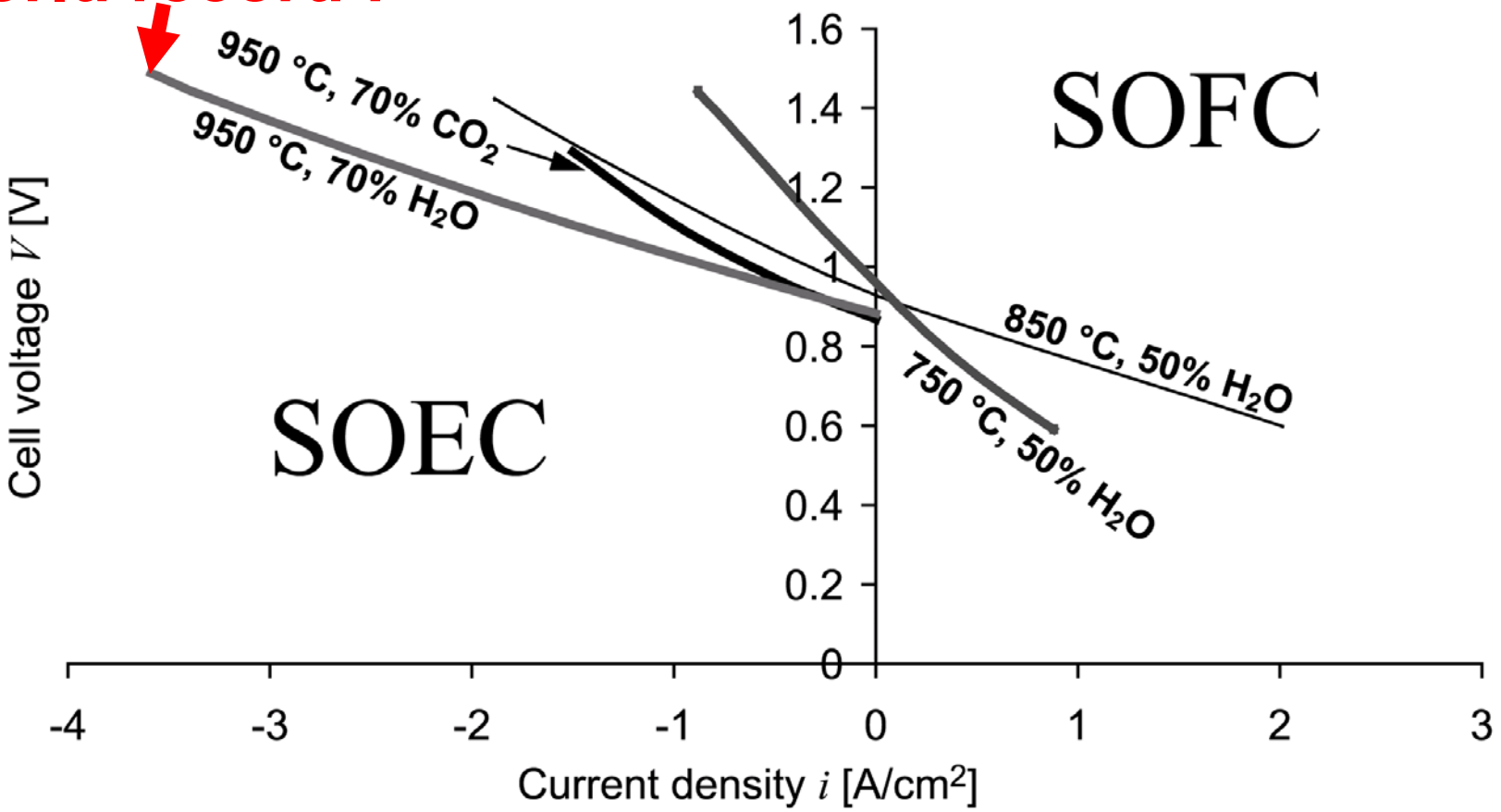
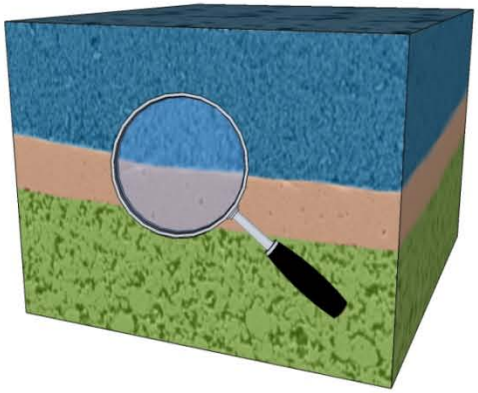
Cell performance DTU Risø 2G cells

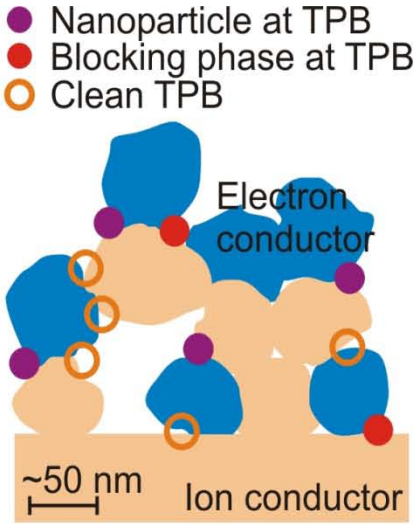
World record !

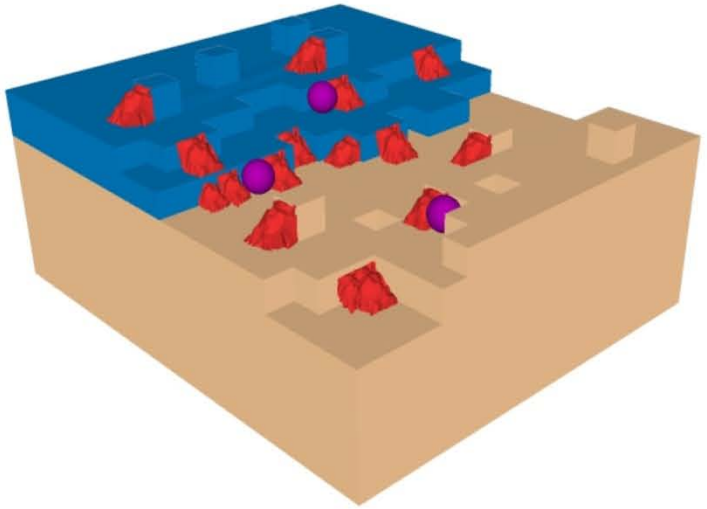


***i* - *V* curves for a Ni-YSZ-supported Ni/YSZ/LSM SOC: electrolyzer (negative cd) and fuel cell (positive cd) at different temperatures and steam or CO_2 partial pressures - balance is H_2 or CO.** S.H. Jensen et al., Internat. J. Hydrogen Energy, 32 (2007) 3253

SOC electrode structure







Solid oxide cell and the oxygen electrode.

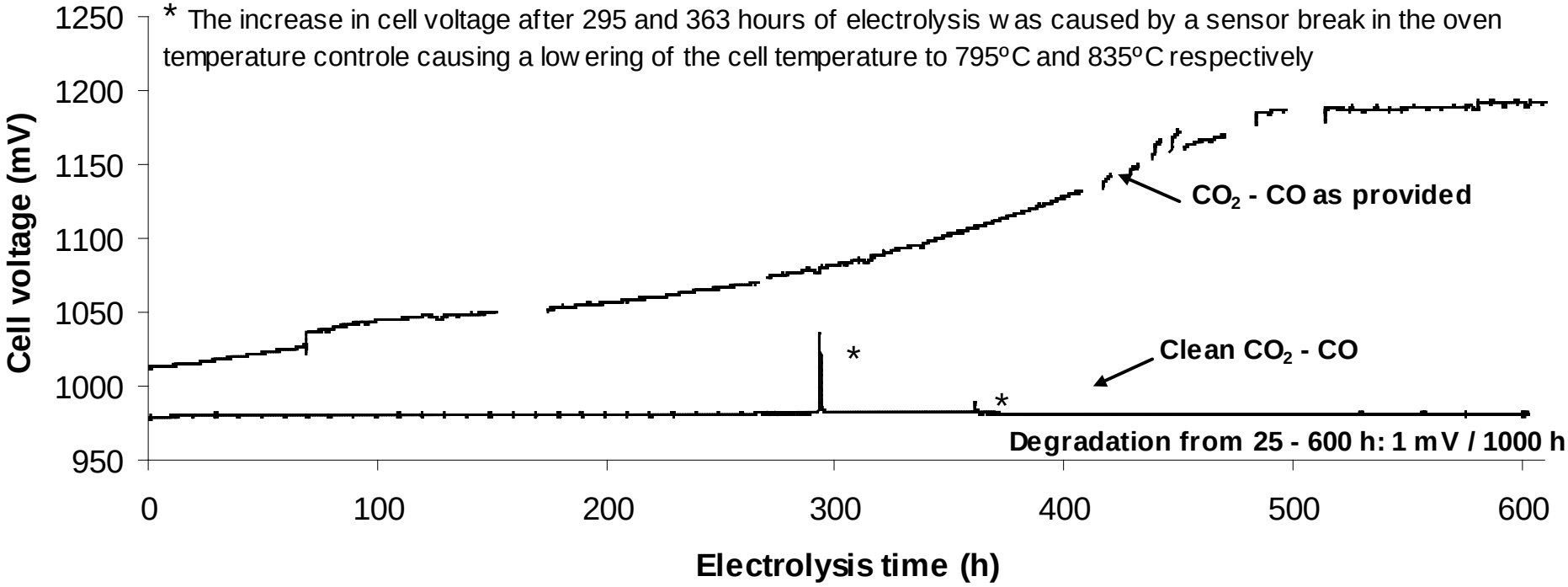
Left: cell structure with 3 thin (10 – 80 μm) layers: fuel electrode (green), electrolyte (beige) and oxygen electrode (blue).

Middle: magnification of composite oxygen electrode.

Right: 3-D picture of how triple phase boundary (TPB) may look on atomic scale. Many different surface sites are possible electrocatalytic active sites.

CO_2 electrolysis - impurities

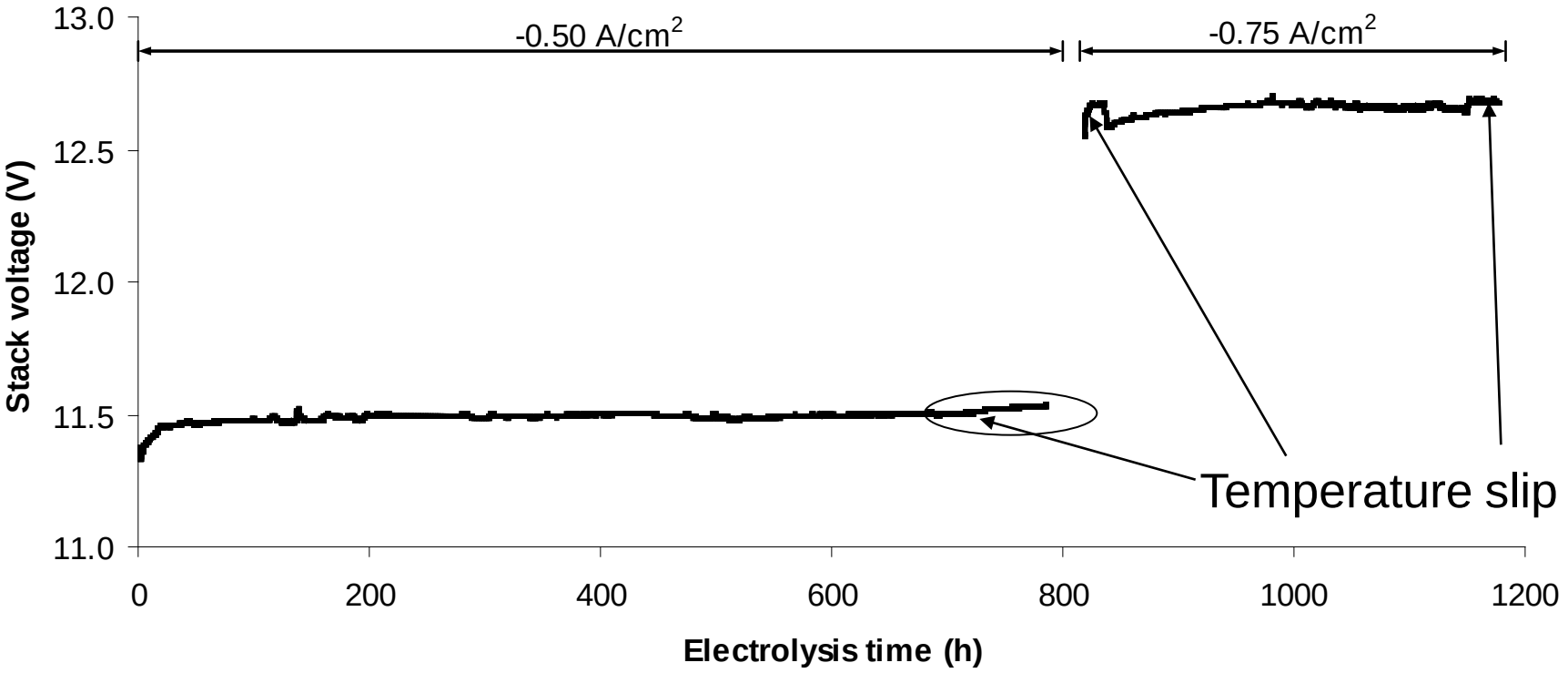
850 °C, 0.25 A/cm²



Only traces of H_2S (pbb level) could be detected in the as provided CO_2 – CO gas mixture

S.D. Ebbesen and M. Mogensen, patent application filed,
Data in ESSL, 2010, same authors

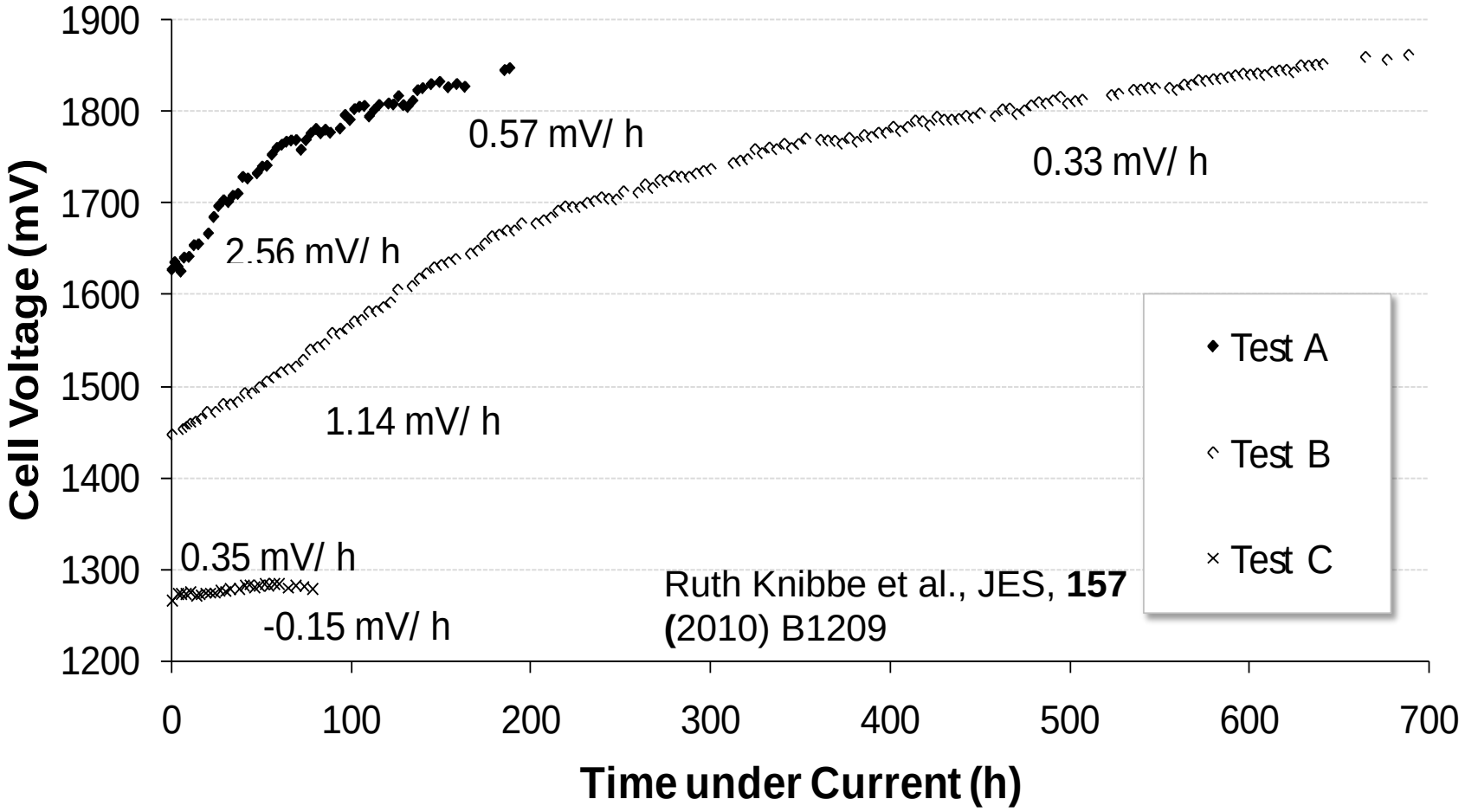
Co-electrolysis H_2O and CO_2
1 kW - 10-cell stack – 12×12cm^2



850 ºC, -0.50 A/cm^2 or -0.75 A/cm^2, 45 % CO_2 / 45% H_2O / 10 % H_2

S. Ebbesen et al., Internat. J. Hydrogen Energy, 36 (2011) 7363

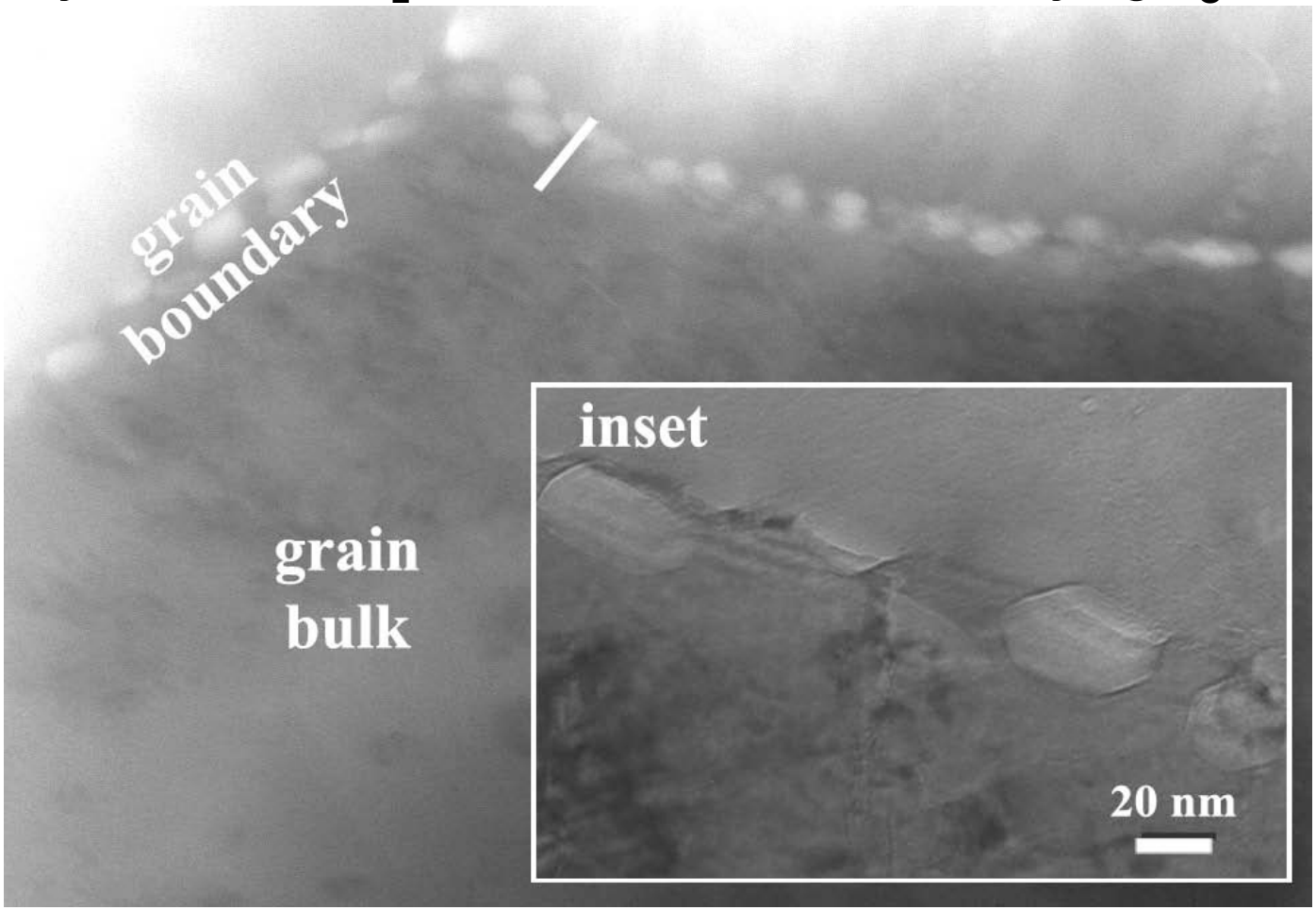
Degradation at high current density



Test A: -2.0 A·cm^{-2}, B: -1.5 A·cm^{-2} and C: -1.0 A·cm^{-2} operated at 850 °C with 50:50 H_2O:H_2

Degradation at high current density

- Much smaller R_p than R_s degradation
- TEM reveals that it is due to O_2 bubble precipitation inside the electrolyte near the O_2 LSM/YSZ-electrode destroying $\sigma_{O^{2-}}$



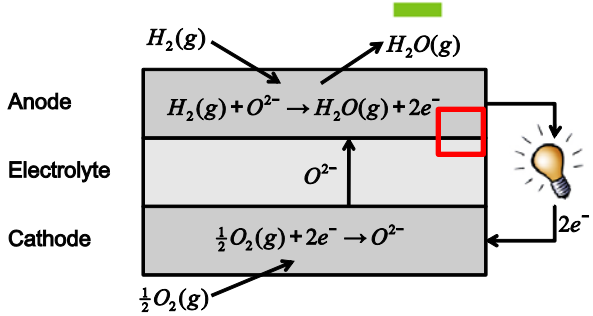
Bubble Formation Mechanism

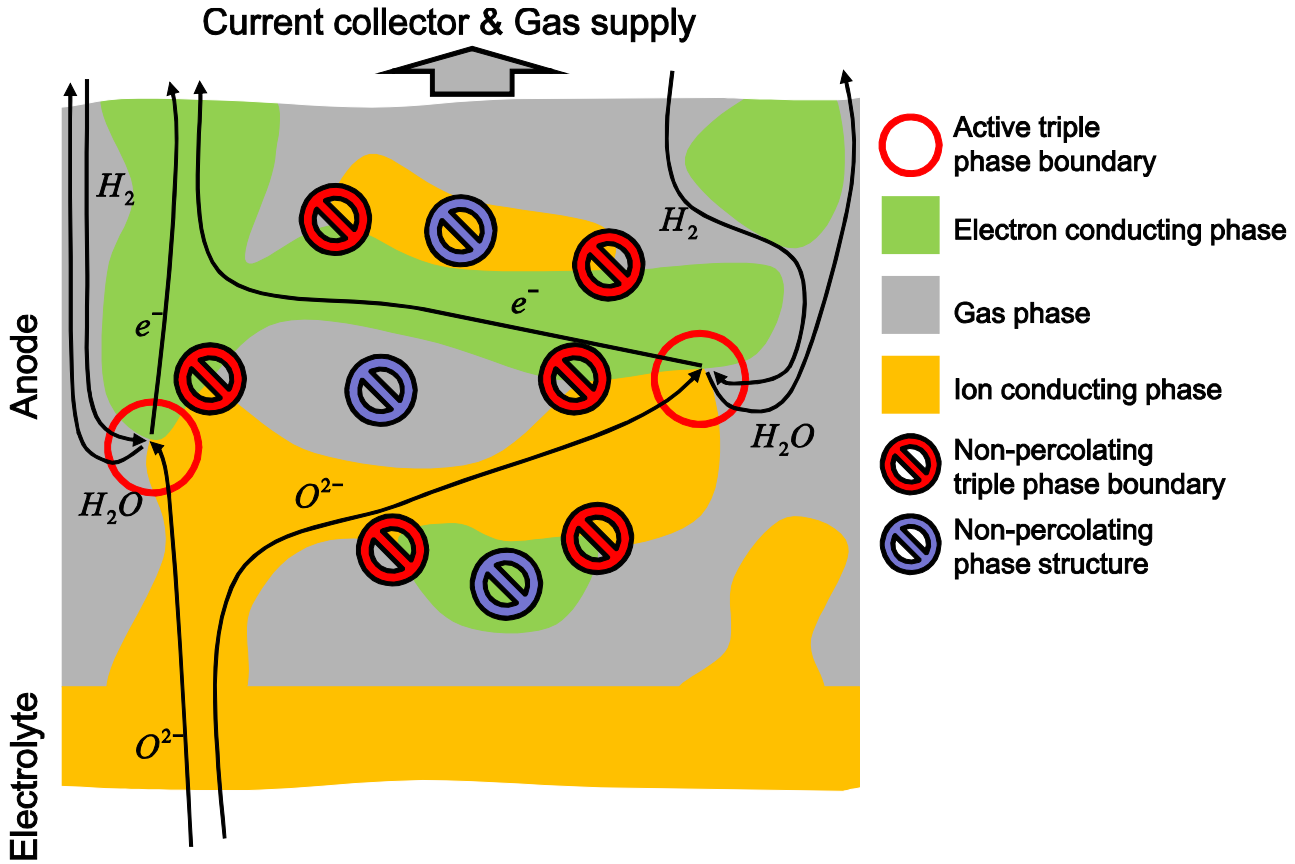
- The anodic (oxidizing) overpotential of the oxygen electrode in electrolysis mode causes an increased potential of electrons inside the adjacent electrolyte
- This in turn causes an increased oxygen equilibrium potential/partial pressure
- 50 mV overpotential $\rightarrow$ 10 bar,
- Oxygen bubbles are nucleated at grain boundaries
- The bubble growth is limited by creep of the YSZ
- Ca. 40 mV overpotential seems allowable, i.e. ca. 1 A cm^{-2} @ 800 °C for 2.5 G cells

The importance of microstructure

We would like to quantify:

- The amount of triple phase boundaries
- Are the TPBs active?
- How long is the pathway to reach them through each phase?
- How wide is this pathway?





Focused ion beam tomography

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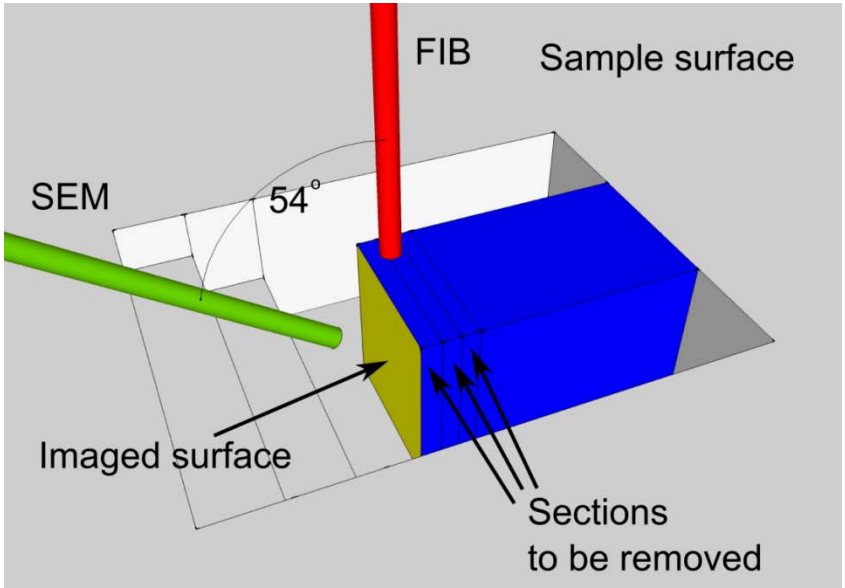
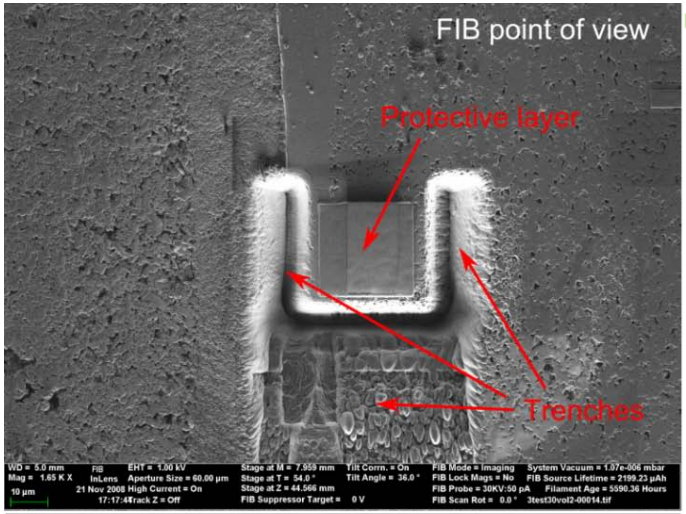
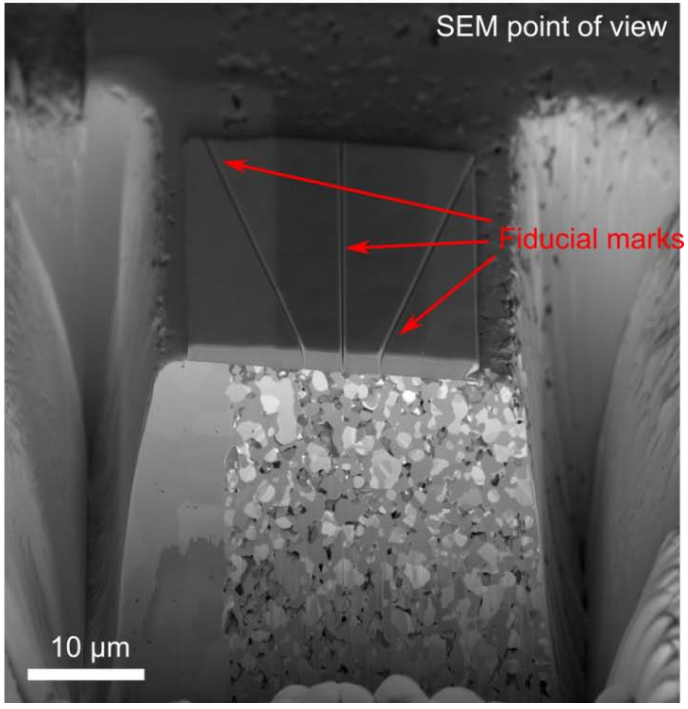






3D rekonstruktion af elektrodestruktur

Motivation – Fuel cells and microstructure

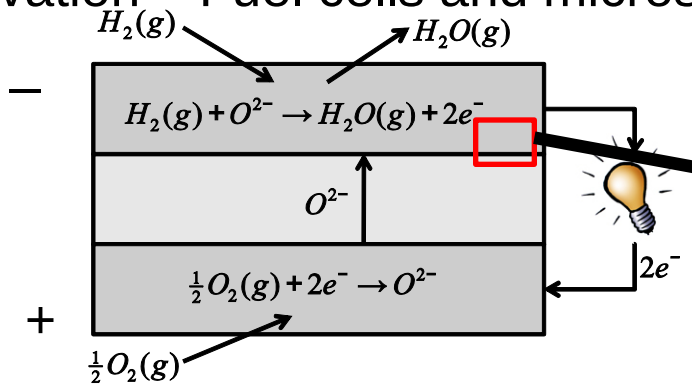
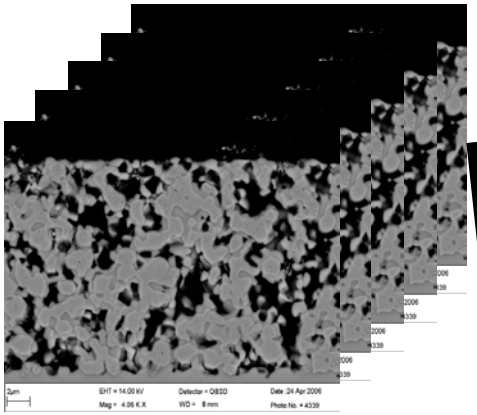
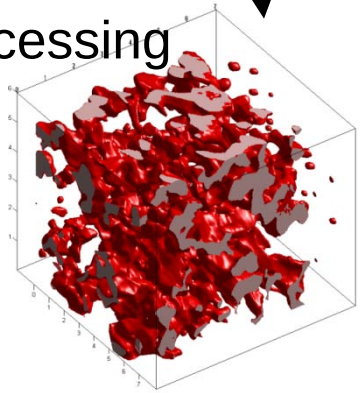


Image acquisition – FIB tomography



Data processing



Parameter extraction

Quantitative values

- TPB lengths
- Surface area
- Percolation
-Tortuosity
- etc.

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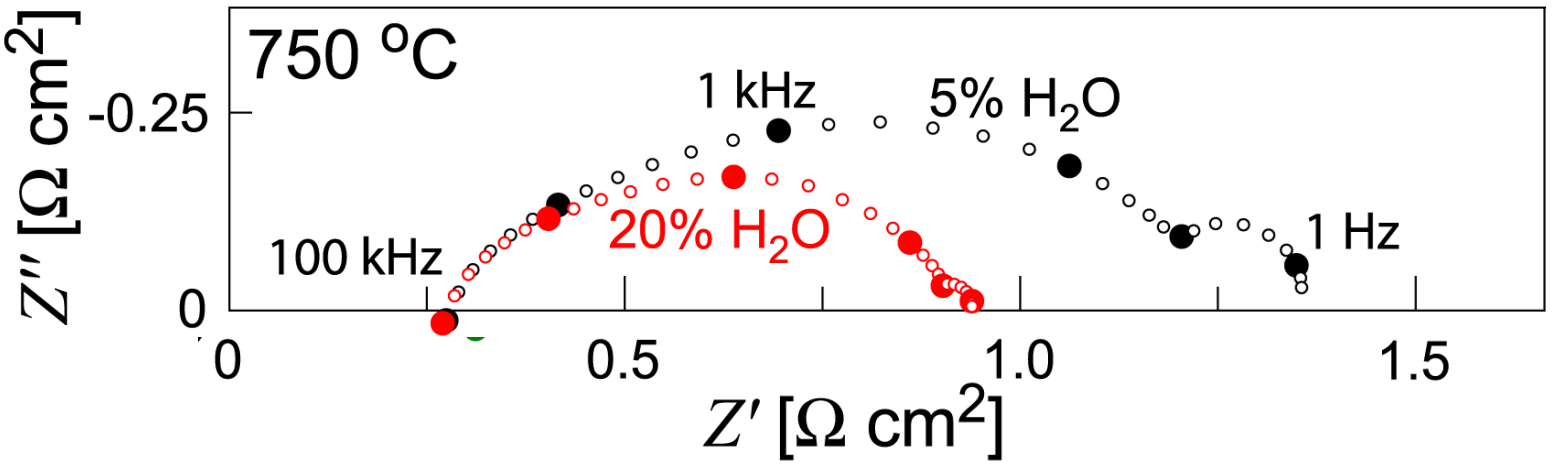
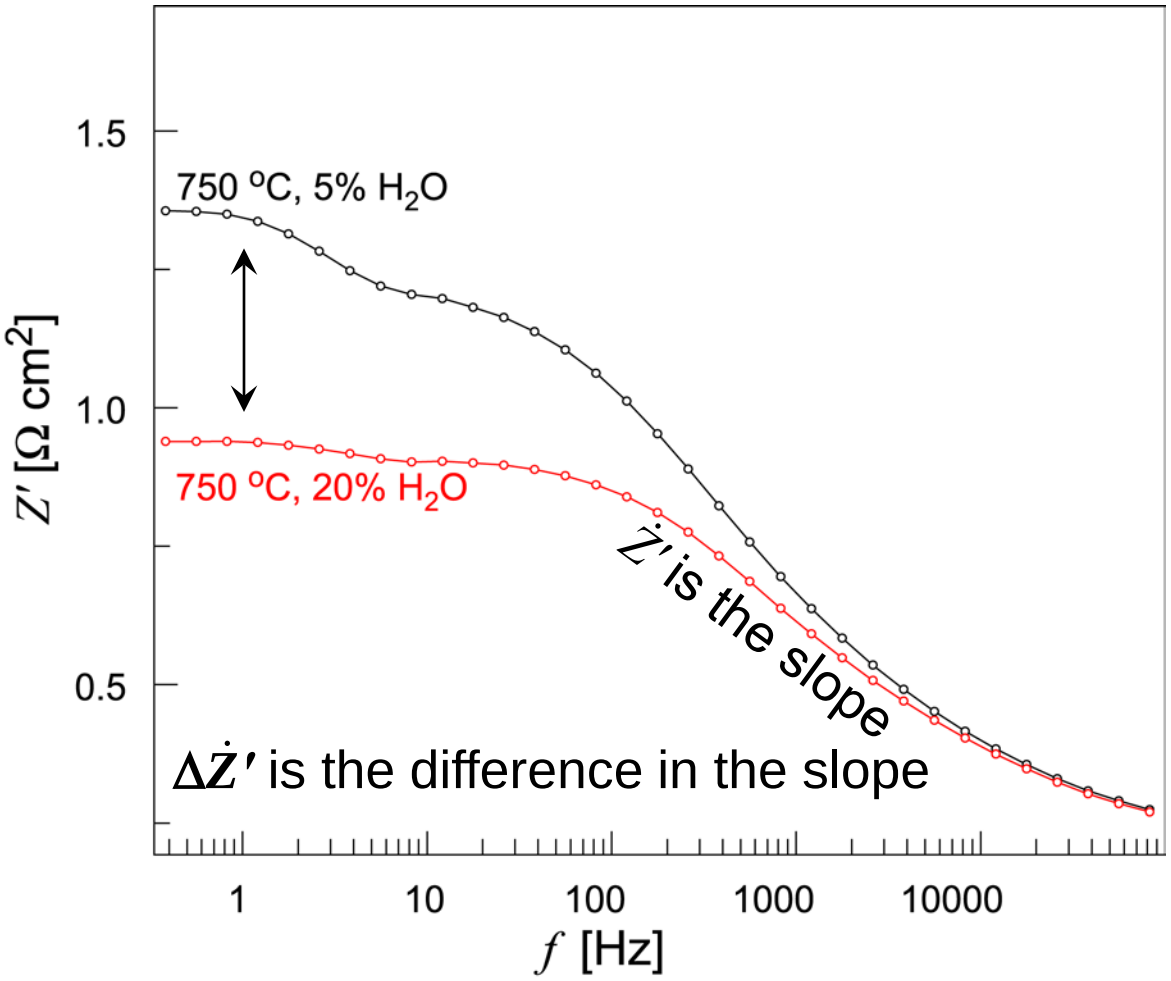
Analysis of Differences in Impedance Spectra, ADIS

Work of Søren Højgaard Jensen, Sune D. Ebbesen, and several more

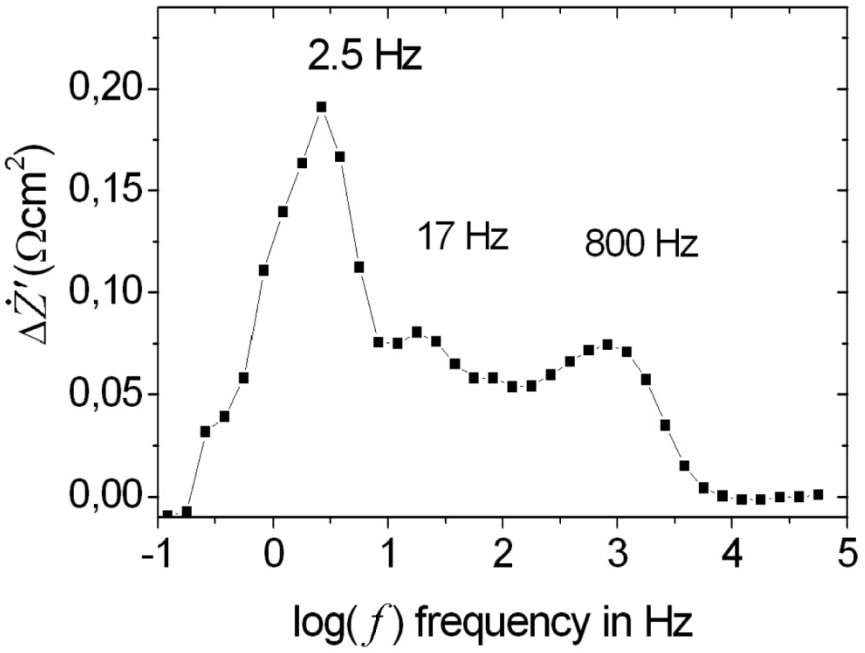
Impedance on a Ni-ZrO2 | YSZ | LSM-YSZ cell



Definition of $\Delta\dot{Z}'$

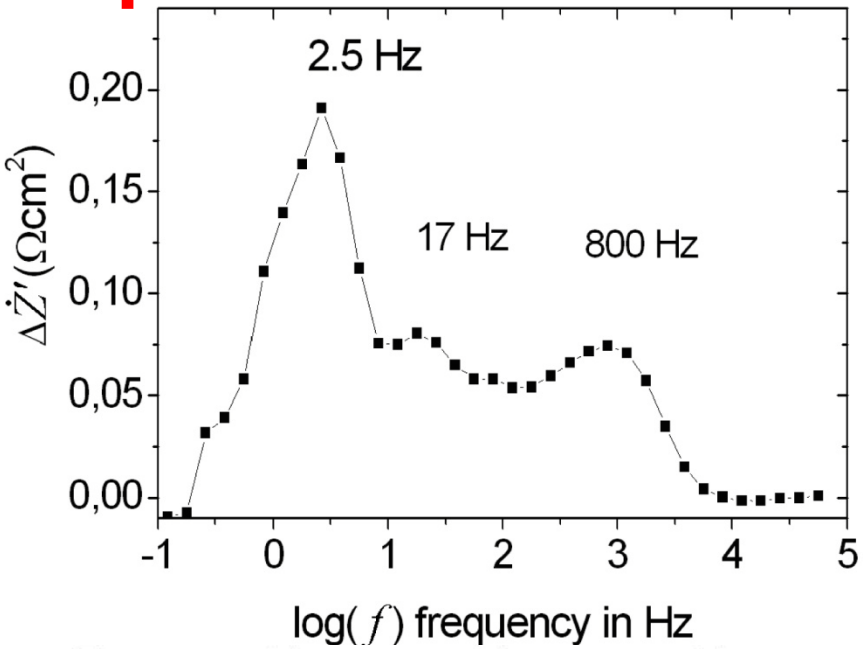


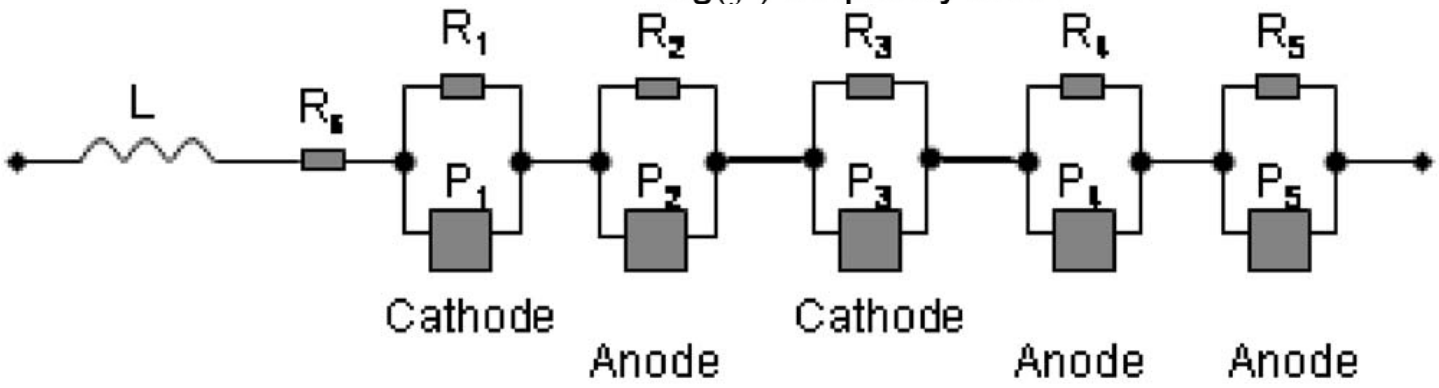
ADIS - Analysis of Differences in Impedance Spectra



The cell impedance obtained for an Ni/YSZ | YSZ | LSM/YSZ at 750ºC
Fuel gas composition of 95% H_2-5% H_2O and 75% H_2-25% H_2O
Air is used as cathode gas.

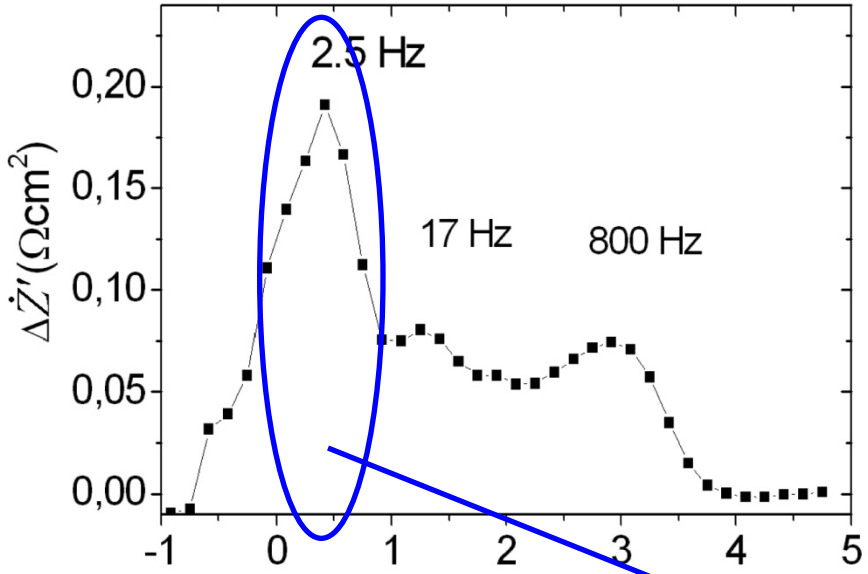
ADIS - Analysis of Differences in Impedance Spectra

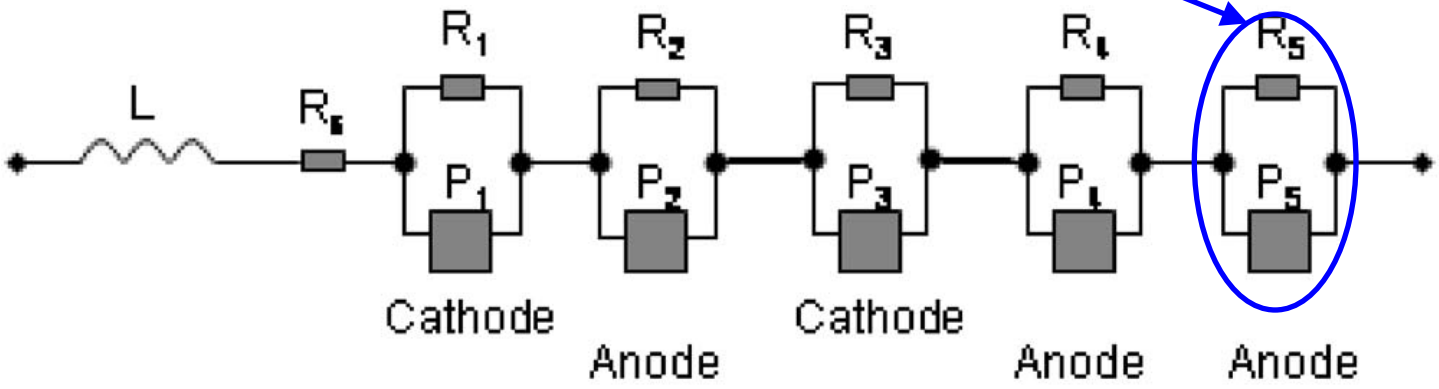




The cell impedance obtained for an Ni/YSZ | YSZ | LSM/YSZ at 750ºC
Fuel gas composition of 95% H_2-5% H_2O (squares) and 75% H_2-25% H_2O (circles)
Air is used as cathode gas.

ADIS - Analysis of Differences in Impedance Spectra





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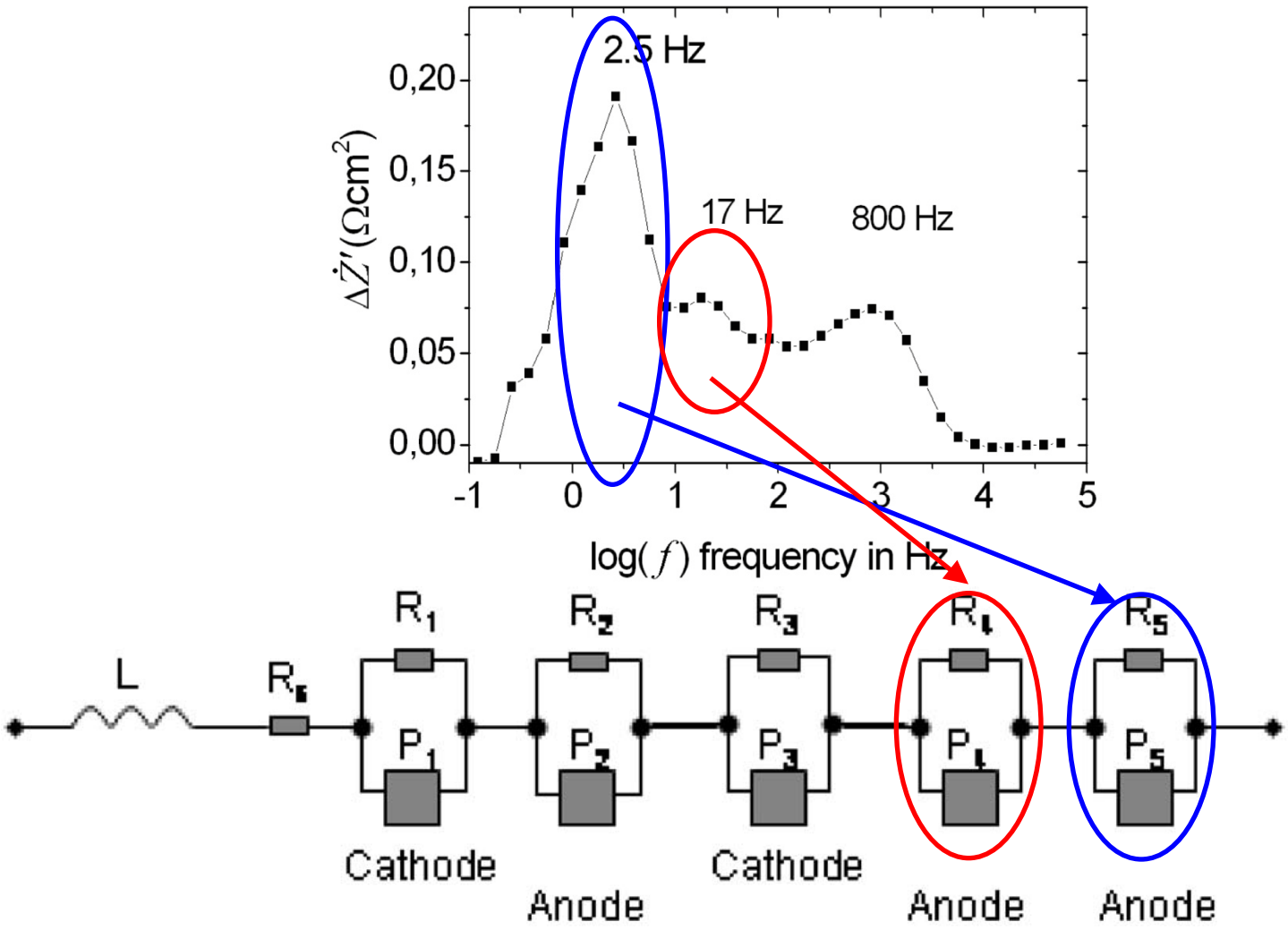

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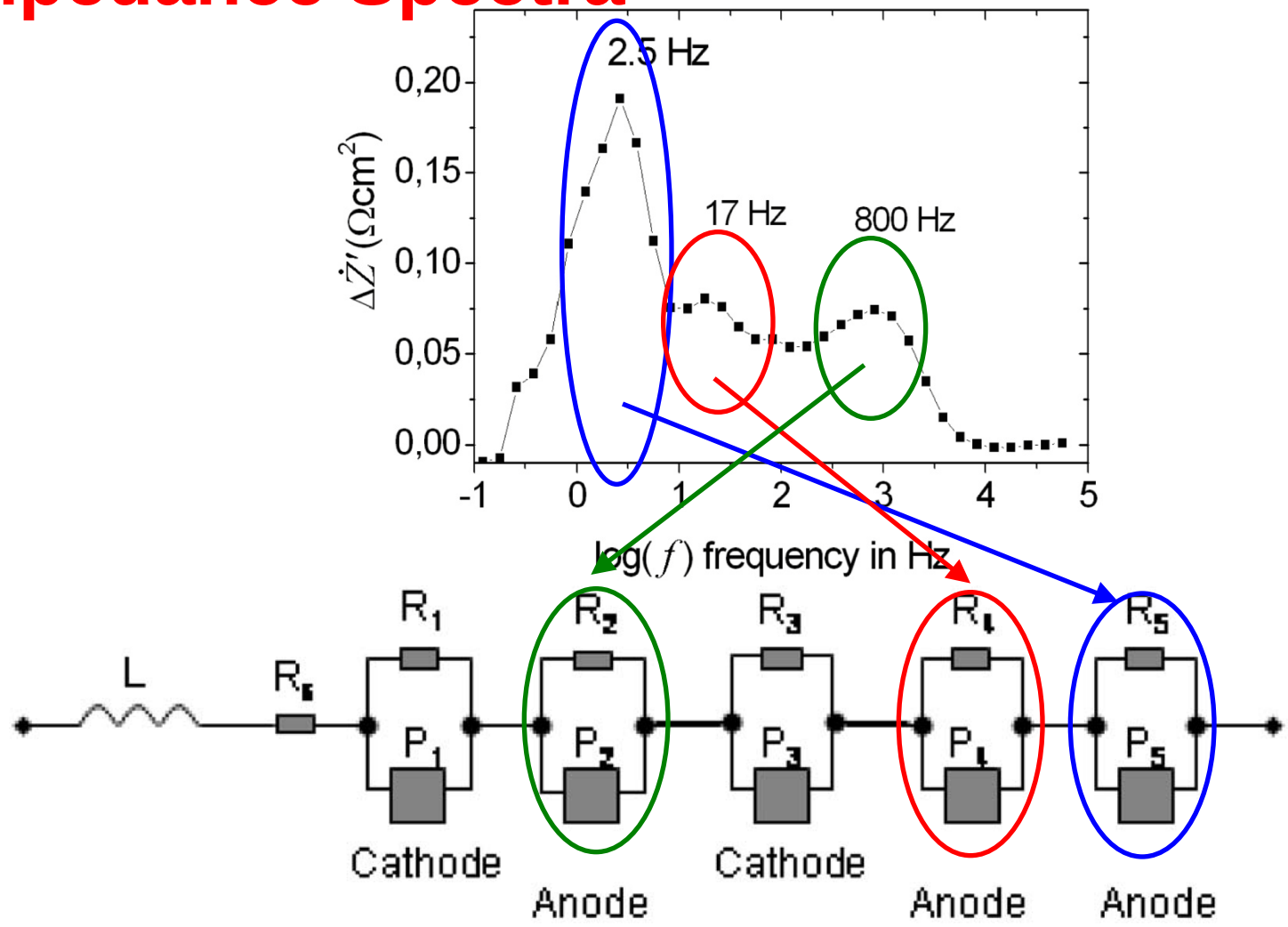

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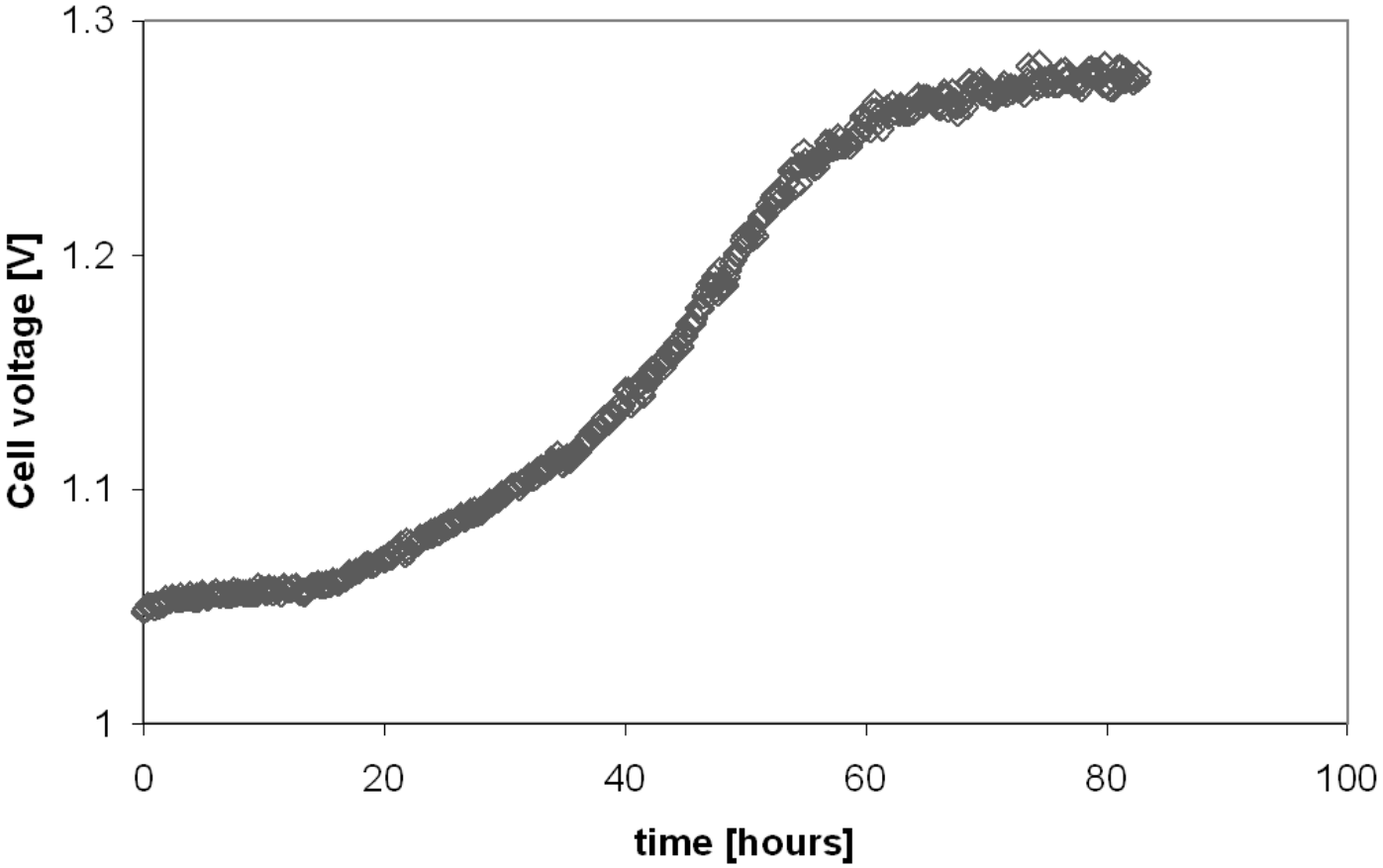
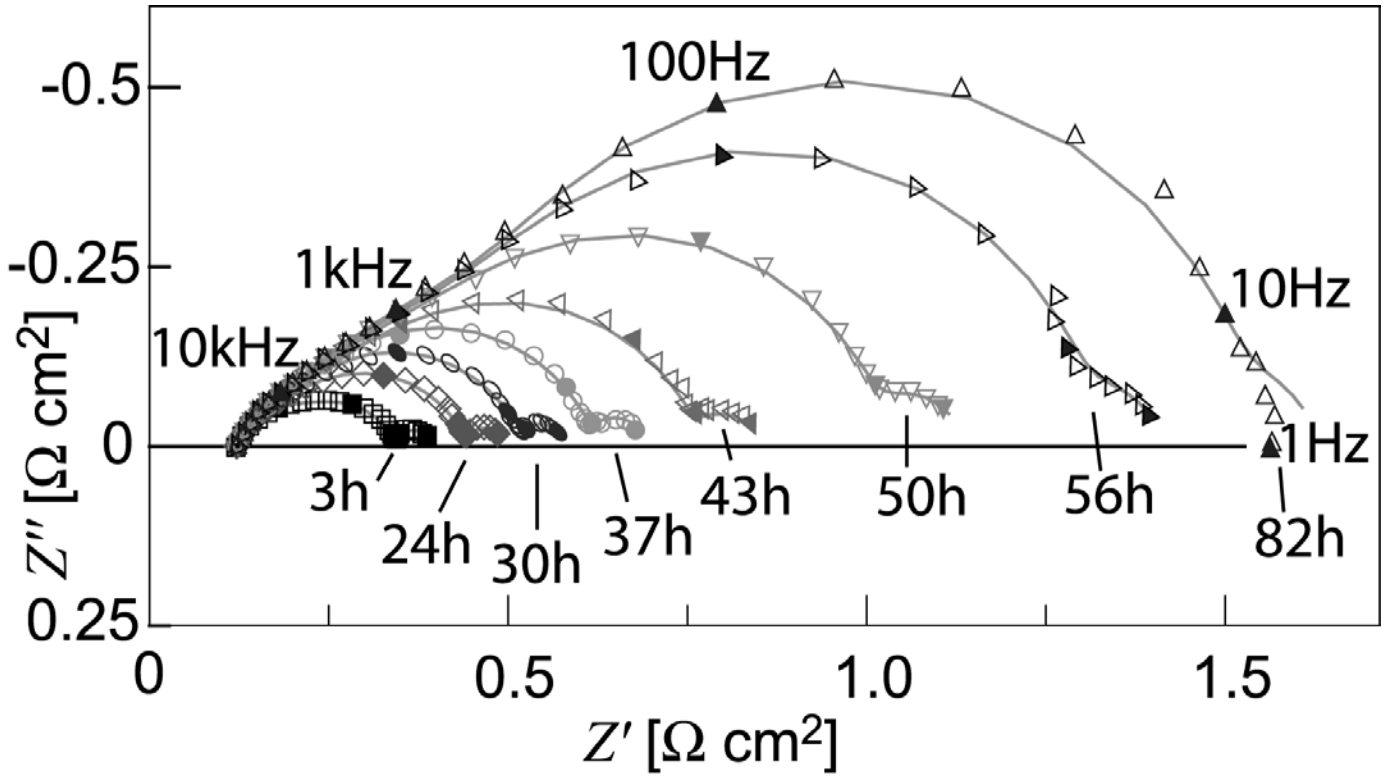
Fuel gas composition of 95% H_2-5% H_2O and 75% H_2-25% H_2O
Air is used as cathode gas.

Performance drop during steam electrolysis operation

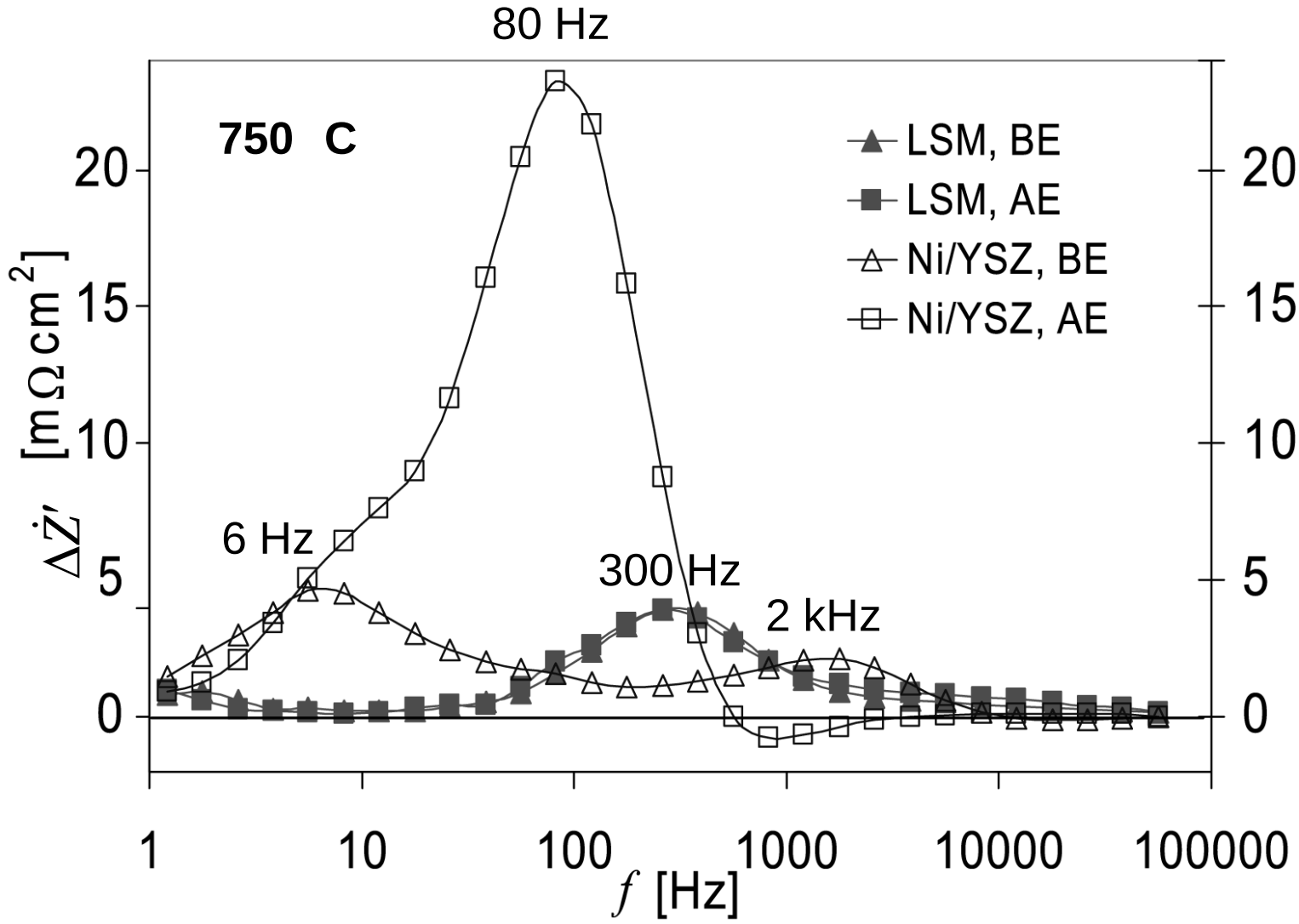


750 C, -0.25A/cm^2, 70% H_2O + 30% H_2

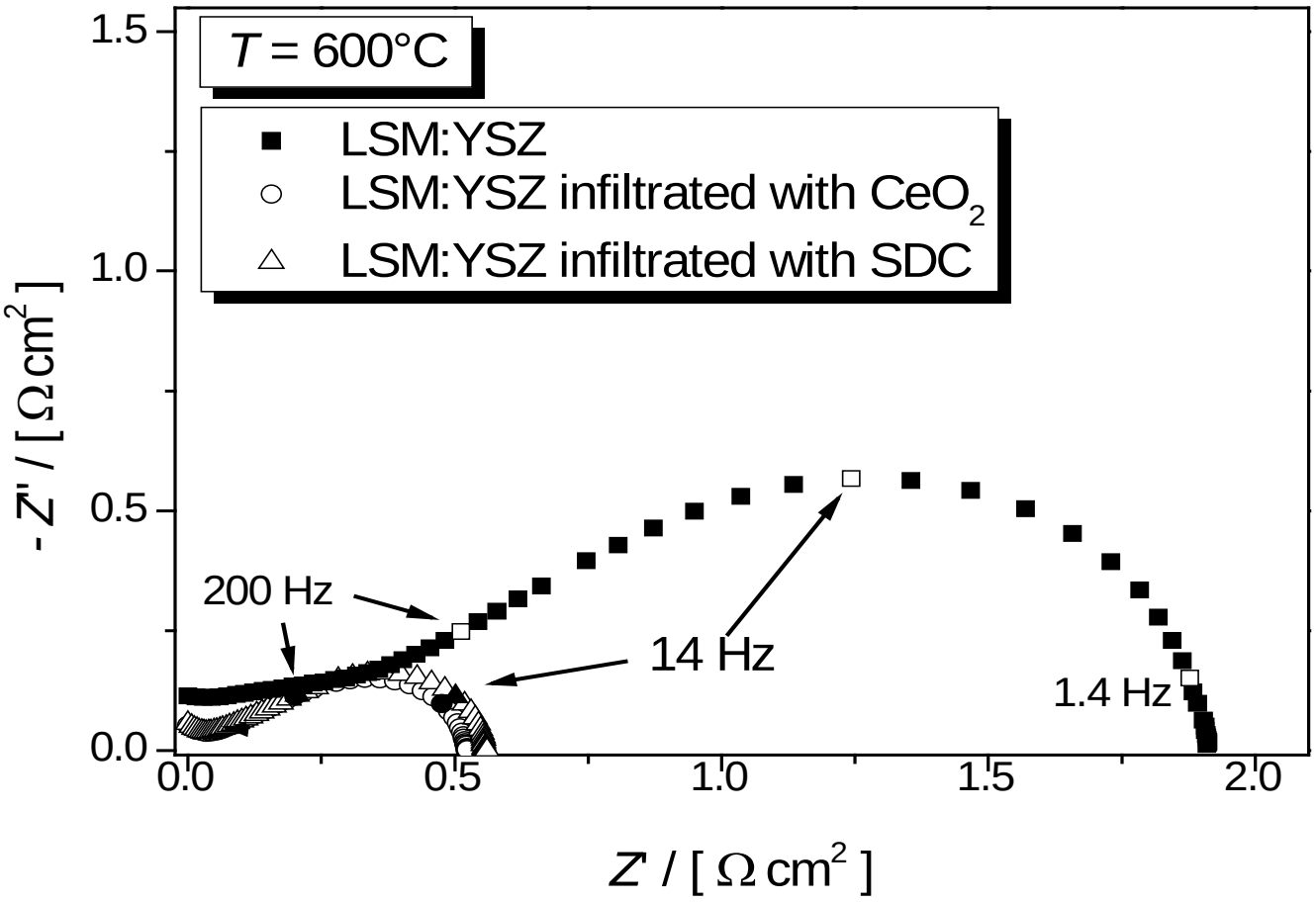
Impedance spectra recorded during electrolysis operation



$\Delta\dot{Z}'$ on both electrodes before and after electrolysis test



Nano-ceria on LSM



EIS of non-infiltrated and infiltrated LSM:YSZ electrodes at 600°C in air

From

SOFC Forum 8: M. Søgaard et al., A0605

Electrode improvements examples

- **The low frequency arc (= the oxygen exchange rate at the surface) is affected by ceria nanoparticles**
- **Ceria nanoparticles in the fuel electrode make it much less sensitive to sulfur poisoning**
- **The effect of nano-particles (good or bad) is a kind of "TPB" effect, i.e. the surface near the TPB of the "coarse" structure of the electrode (the "original" electrode) is affected by some kind of interaction/reaction with the nano-particles**

- **The interaction with impurities is probably important (scavenging)**

- **Other TPB chemistry may be important. We do not know much about the details.**

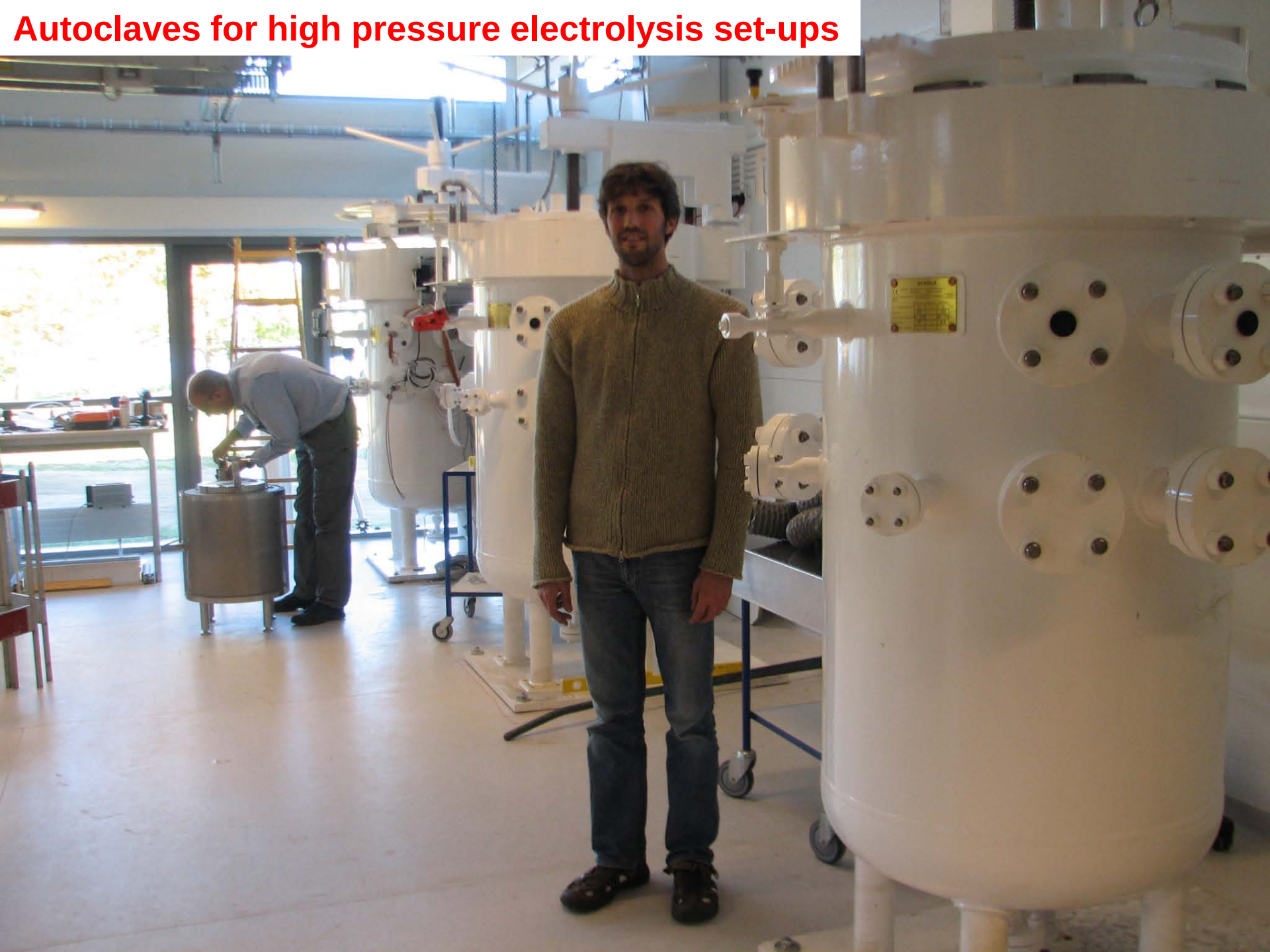
- **New surface sensitive *in situ* methods are urgently needed**

New facilities in cooperation with other projects

- **“Electrochemistry under elevated temperature and pressure” established - 5 experimental set-ups (co-financed with several projects) with pressures up to 95 bar with several relevant gases. 3 are in operation and remaining 2 to be finished by end of 2012.**

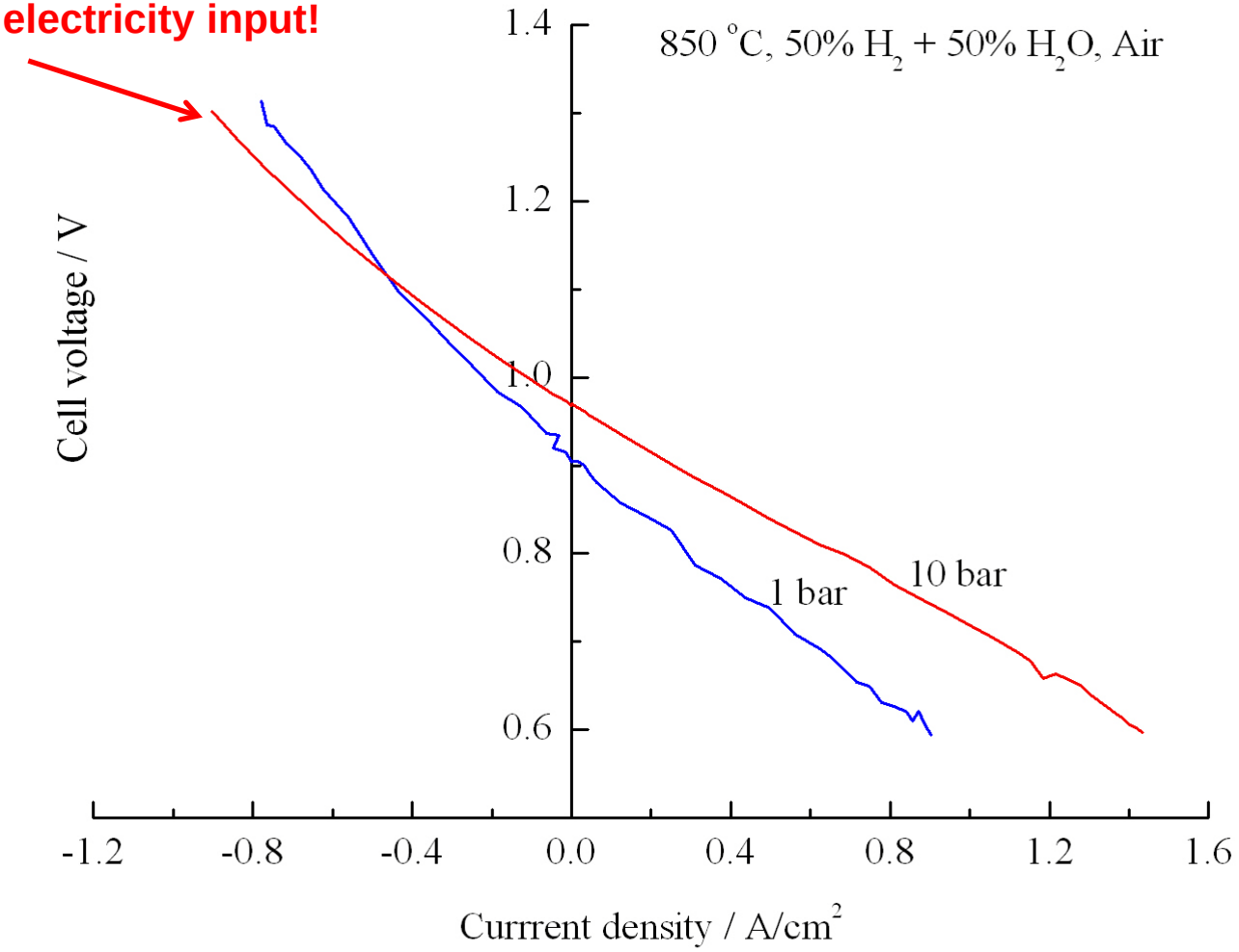
- **“In situ electrochemistry on micro and nano scale” - novel custom made equipment - CAHT-SPM (controlled atmosphere high temperature scanning probe microscopy) - established in cooperation with Danish Micro Engineering A/S. In-situ electrochemical investigations on scales from nanometer up to 50 micrometer scale.**

Autoclaves for high pressure electrolysis set-ups



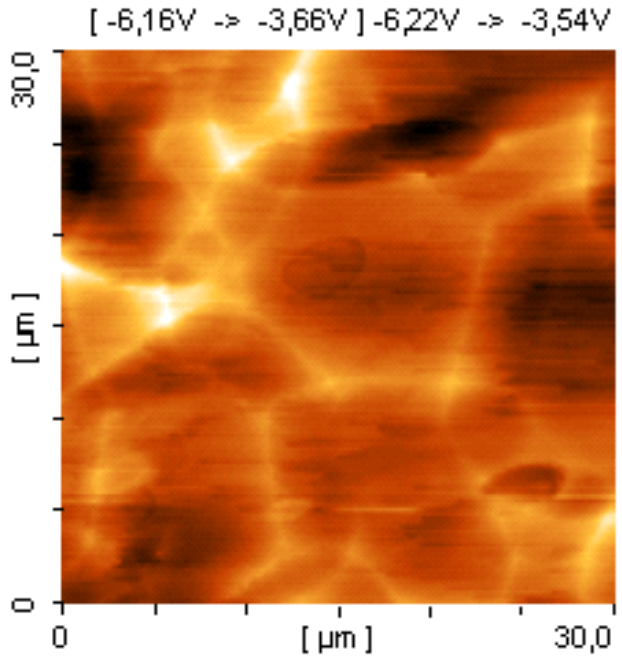
Effect of 10 bar pressure

We get pressurized hydrogen with lower electricity input!



New in operandum technique

CAHT-SPM *in situ* measurements of electrochemistry at high temperature



Surface and grain boundary conductivity at 650°C image of YSZ electrolyte with 1000 ppm Si. White is high resistance.

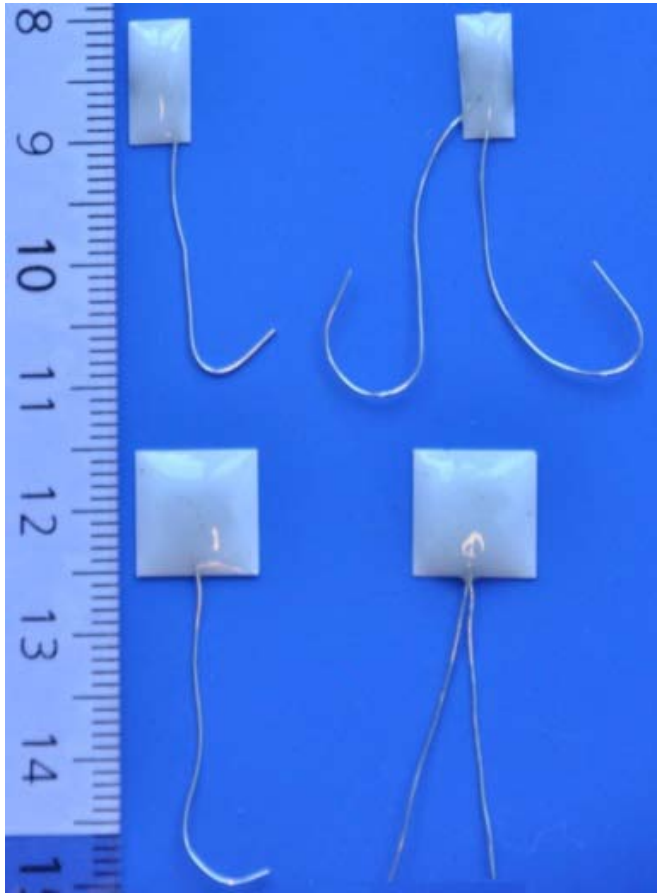
Oxygen sensor med indbygget Ni/NiO reference elektrode

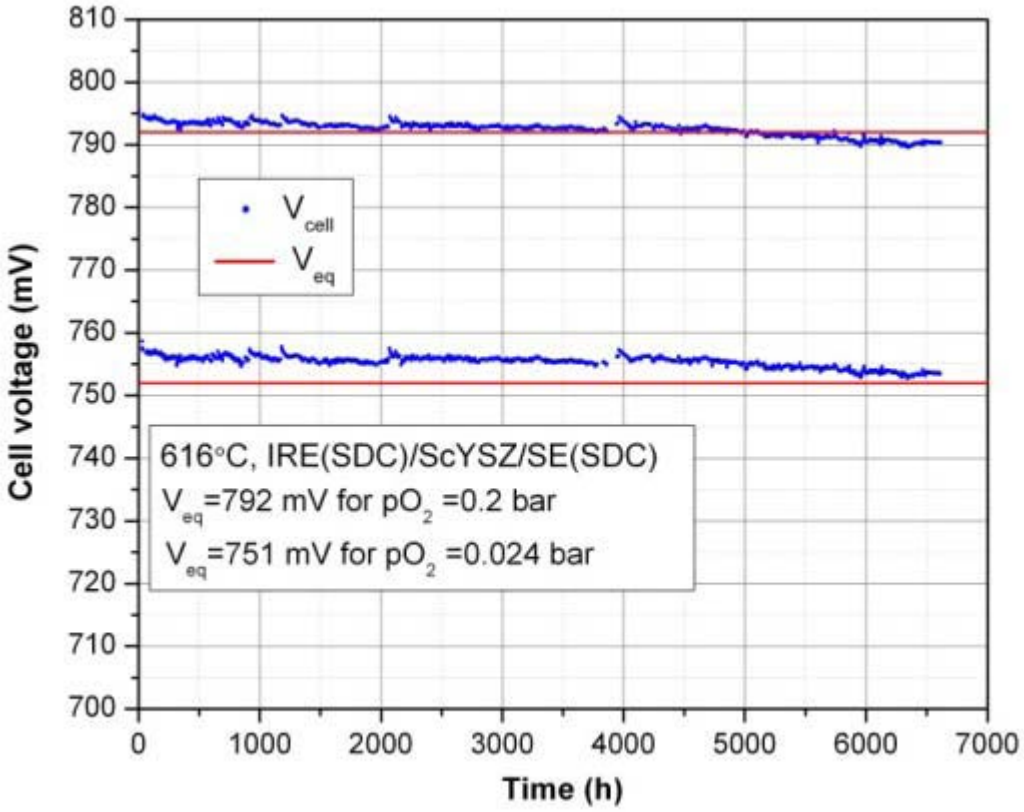
Efter gennemførelsen af det første SERC del-projekt omkring forbedring af oxygen sensorer, fik vi den idé at vi kunne lave en anden type sensor med intern reference i stedet for den traditionelle med tilførsel af en reference gas

Et PhD - projekt blev startet og det er lykkedes at fremstille en meget kompakt lille sag, der virker fint

Der er indleveret en patentansøgning

Oxygen sensor med indbygget Ni/NiO reference elektrode





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Publications and communications

- 69 articles in international journals and books so far
- 12 more in press, submitted or close to finished, most will be submitted in 2012
- ?? more to come
- 8 PhD theses
- 4 MSc and 1 BSc theses
- 2 Patent applications
- Many conference participations (> 40) and contributions to workshops - also co-arrangements. Many invited presentations e.g. IGU's World Gas Conference, Kuala Lumpur, Malaysia, June 4- 8, 2012, "Green Gas" talk.
- 12 Biannual meetings + broad public meeting next Thursday
- web-site: www.serc.dk

Opfyldelse af mål

Der blev opsat 12 milepæle om komnkrete mål, der skulle nås.

De 11 er blevet nået helt, og 1 næsten. Den sidste vil meget sandsynligt blive nået i et af de nye projekter næste år.

Disse milepæle er mest for "nørderne". Den seneste SERC årsrapport, der beskrive dem og graden af målopfyldelse, kan findes på SERC hjemmesiden

www.serc.dk

Fortsættelse af aktiviteterne

- **Topsoe Fuel Cell A/S og Topsøe A/S fortsætter kommercialiseringen af SOFC of SOEC, men der stadig hårdt brug for strategisk forskning på området.**

- **Projekter (NEC og EUDP) inden for SOEC til syntetisk brændsel (tryksætning, levetid) og opgradering af biogas med SOEC er bevilget og startet.**

- **Ansøgninger om projekter til studier af forskellige aspekter af TPB - regionens kemi og struktur er sendt.**

- **Der er mindre aktiviteter finansieret af DTU i gang.**

Review

- When all guests and colleagues that have been clearly involved in SERC in some way are included, it adds up to more than 60 persons.
- SERC has been carried out in close cooperation with other related projects and activities in the participating companies and university departments.
- We have put emphasis on cooperation/synergy between the sub-projects and activities within SERC.
- We have put even more emphasis on close cooperation with other running projects. A basis for several papers and for one the patents was made in other projects, but as these projects were small/short, the were not resources to take the scientific work into publications. As the work was well related to SERC, it was finished within SERC.

Review cont.

- **SERC was based on already existing visions shared by the departments and some of the companies**

- **This (and other common interests) has resulted in big extra contributions, in particular from DTU Energy Conversion (prev. Risø DTU); considerable man-power and cash money from outside SERC have been contributed to build-up new applied (strategic) research facilities**

- **This means on the other hand that SERC money and results will have a very large future impact in addition to the results already achieved**

Alle de andre resultater

- **Der er fundet/opdaget et hav af små, men tilsammen særdeles betydningsfulde detaljer, som der ikke er tid til at fortælle om idag.**

- **Dem kan man læse om i de publicerede artikler.**

- **Der er en opdateret liste over publikationer på hjemmesiden**

www.serc.dk

Konklusion

- **The mission is fulfilled**
- **The main impact of SERC may occur in the future**

Tak for jeres opmærksomhed